THE OHIO STATE UNIVERSITY

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Rheological Characterization of PHBV Systems to Quantify Their Processing Capabilities in Packaging Applications

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1 Abstract

The extensional rheology of PHBV (PURE) and 3 PHBV compounds previously synthesized by Zhao: w/15 wt% natural rubber (15NR), w/NR and 3 PHR peroxide curing system (PEROX), and w/NR+peroxide and 4.2 PHR coagent (COA), previously synthesized by Zhao was characterized using a unique methodology approach to overcome the challenges associated with measuring extensional flow using a lower molecular weight, and consequently lower viscosity material, PHBV (Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)). To overcome temperature control ambiguity, a lumped system analysis was conducted to approximate the sample's temperature based on the oven temperature reading and thermal properties of PHBV retrieved from the literature. To validate the assumptions associated with using a lumped system analysis, the sample's Biot number was calculated and found to be less than 0.1 for all sample thicknesses, satisfying the requirement of having a uniform sample temperature. To present these calculated sample temperatures at the same temperature to allow for meaningful viscosity comparisons, dynamic shear data was collected on the same compounds to obtain shift factors using the WLF equation and the principle of time-temperature superposition. Because only one of the compounds successfully fit the WLF equation to its shifted data, the WLF constants $C1$ and $C2$ calculated for that compound were used for all the others as an approximation. The transient extensional viscosity data was shifted vertically and horizontally based on these shift factors and compared to transient shear viscosity data to quantify the degree of strain hardening in each compound for each extension rate. At the high stretching rate of 10s-1, the compounds exhibited the expected pattern based on the amount of long chain branching/crosslinks in their structure, with PHBV showing the least followed by 15NR, PEROX, and finally COA showing the most strain hardening. This extensional rheology characterization can be applied to any new compounds of interest in food science and biodegradability to evaluate their potential in applications that would require film blowing or blow molding, such as food packaging.

Dedicated to my Supportive Friends and Family

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2.1 Literature Review

2.1.1 Introduction to PHBV

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Figure 1), is a bio-derived thermoplastic that is being explored as a substitute for common petroleum-derived thermoplastics such as polypropylene and polyethylene. Specifically, when the poly-3-hydroxyvalerate (HV) portion of the backbone is 3-8 mol%, PHBV has similar thermal and mechanical properties to polyethylene[6].

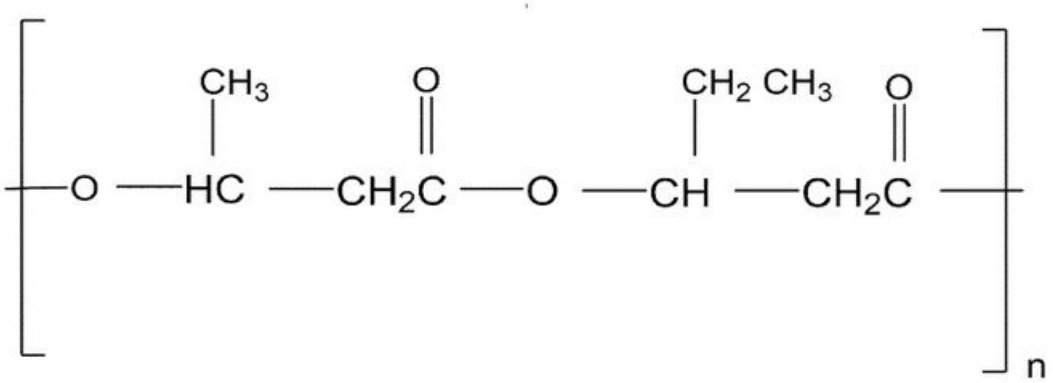

Figure 1: Structure of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) [1]

Additionally, as PHBV is a Poly(hydroxylalkane) (PHA) that is made from the bacterial fermentation of starch, it sees applications because of its biodegradability and biocompatability[6]. However, its brittleness and high thermal sensitivity to degradation hold it back from industrial use[6]. For example, pure PHBV melt temperatures range from 170°C to 180°C, but PHBV at various hydroxyvalerate concentrations has been found to degrade from β-elimination of the ester bond above 160°C[7],[8]. Improving these properties is an important field of study as it could help the plastics industry become less petroleum dependent by introducing a new, more renewable source of raw materials that also improve global sus-

tainability. Consequently, other strategies to improve PHBV properties have been explored through filler incorporation in the form of plant fibers[9] as well as fumed silica[10]. Other polymer systems have been explored to see their potential in improving PHBV performance, such as poly-lactic acid (PLA), but they were largely immiscible with the PHBV phase[11].

In a recent thesis completed by Xiaoying Zhao at The Ohio State University, Zhao blended high molecular weight (HMW) natural rubber (NR) with PHBV to help with deficiencies of PHBV, specifically its brittleness and small processable temperature range[12]. For polymers to blend together uniformly, their viscosities should be similar. To achieve similar viscosities, Zhao selectively crosslinked the HMW NR using a peroxide curing system at various peroxide concentrations, while blending it with the PHBV in a twin-barrel extruder, to observe which peroxide system/concentration yielded the best blend[12]. By comparing complex viscosity frequency sweeps to pure PHBV, Zhao concluded that the optimal combination was SMR-L (Standard Malaysian Rubber Grade L) with 2 phr (parts per hundred rubber) Luperox 101XL45 peroxide[12]. Then, various concentrations of NR were blended with PHBV to determine which yielded optimal mechanical and rheological properties that overcome the drawbacks of PHBV as a substitute for petroleum derived thermoplastics in packaging applications. SEM (Scanning Electron Microscopy) images were taken of these various NR concentrations to see how the crosslinking morphology was changing. These images suggested that not all crosslinking occurred between the NR chains, but some NR/PHBV crosslinks formed as well[12]. From the study, Zhao recommended a blend with 10-15 NR[12]. Another work by Modi et al. investigated these PHBV/HMW NR systems but took a simpler approach by working with non-crosslinked HMW NR rather than attempting to crosslink it during the blending process[13]. This study also found that the degradation of PHBV as it exceeds its melting point is greatly diminished by the improved heat dispersion from the presence of the NR in the blend[13].

Natural rubber was used to develop these PHBV composites because it is also derived

from a natural, sustainable source[2]. Because of its elasticity and low cost, it would be an economically viable additive to validate the commercialization of PHBV composites if successful. Zhao analyzed the underlying mechanisms as to why blending with natural rubber specifically resulted in improved toughness, citing void toughening theory and stress field theory[2]. Zhao continued to improve the PHBV blends by using the coagent, Trimethylol propane triacrylate (TMPTA). In her previous work, she found that side reactions were more kinetically favored with the selected peroxide curing system when there were few reactive sites on the polymer. Coagents such as TMPTA add more reactive sites to the composite during the curing time, allowing for more crosslinking to occur, outlined in the mechanism seen in Figure 2[2].

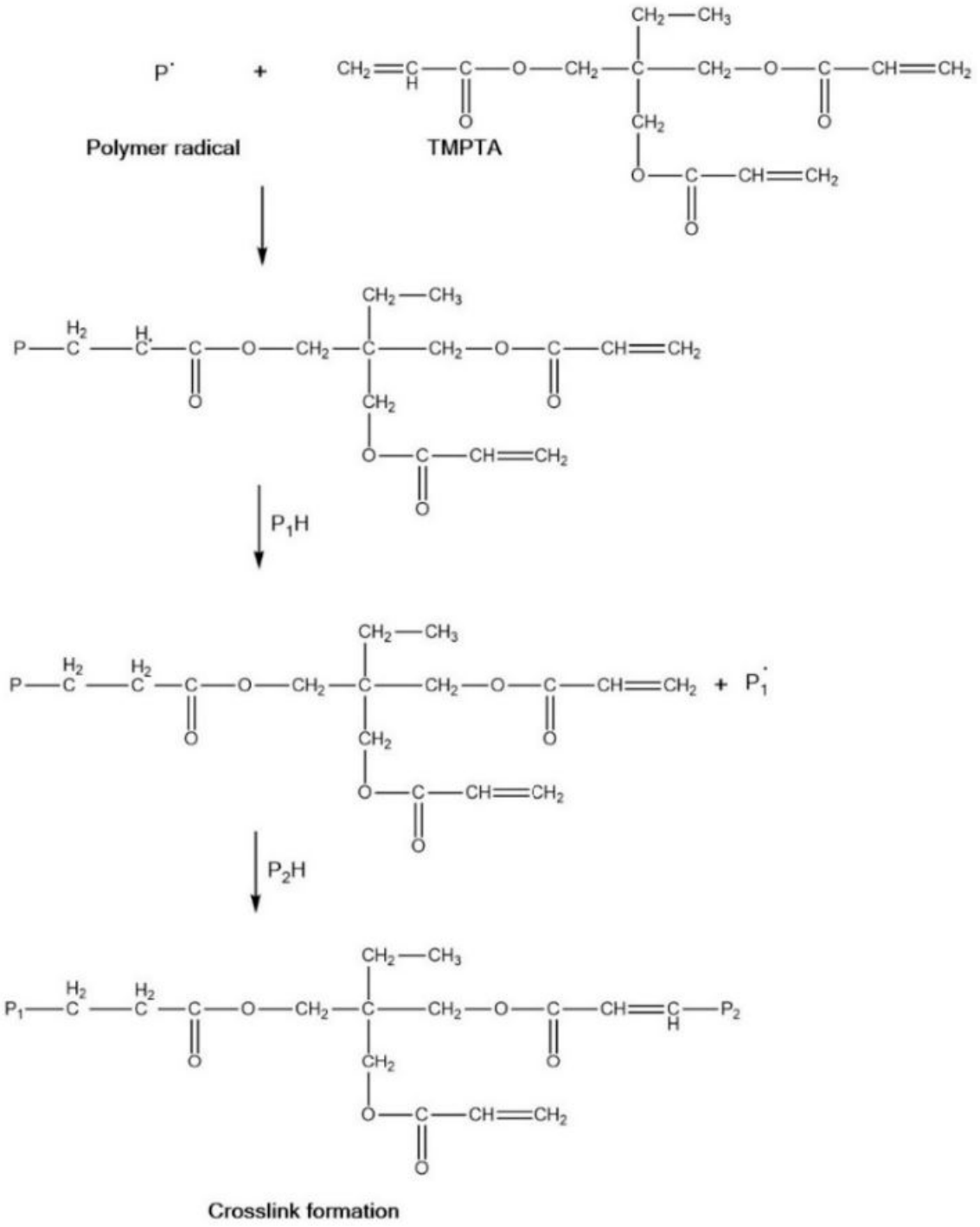

Figure 2: Mechanism by which TMPTA Coagent Increases Polymer Crosslink Density [2]

By using measurements of the gel fraction of the crosslinked polymer, the crosslink density for each composite was determined. Ideally, all of the natural rubber in the composite (15 weight %), would crosslink, so the weight percent of the gel should be close to 15%. While the composite that only had the peroxide curing system achieved a gel content of only about 6%, the composite that used a peroxide system in combination with the TMPTA coagent exhibited a gel content of about 13%, much closer to the wt% of the original natural rubber in the blend[2]. This drastic difference in crosslink density demonstrates the increased higher order structure of the polymer matrix in the composites with the coagent. The composite with only the peroxide curing system also showed more gel content than the composite with no curing (about 4% gel), which showed more that neat PHBV (0% gel)[2]. This thesis aims to extend this finding by demonstrating that the increased gel content and consequently higher order structure results in more entanglement behavior that would cause strain hardening in an extensional flow.

2.1.2 Introduction to Extensional Rheology and Application

Rheology is the study of material flow and deformation and sees applications in many industries due to the need to describe unique solid/fluid behavior, including but not limited to: polymers/plastics, paints, tires, petroleum, and cement. A Newtonian material's deformation can be predicted by Newton's law of viscosity, where viscosity is a constant, see Equation 1.

$$\tau = \eta\dot{\gamma} \tag{1}$$

At low strains and strain rates, even non-Newtonian materials exhibit constant rheological properties, such as viscosity. This region of low strains is called the linear viscoelastic region, where viscoelastic is used to describe the non-Newtonian behavior of polymers that results from their time-dependent deformation response to an applied stress. When above the highest strain/strain rate in the linear viscoelastic regime, the material is in the non-

linear viscoelastic region, where it starts to exhibits deviations from the constant behavior in the linear-region. When a shear deformation is applied, most polymers exhibit a drop in viscosity at high strains/strain rates, described as a shear-thinning response (Figure 3), due to the reduction of entanglements upon stretching.

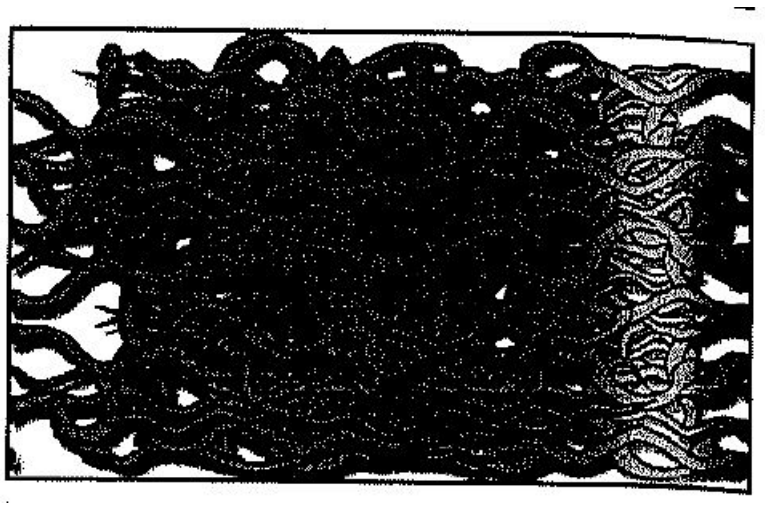

Figure 3: Shear-Thinning in Polymer Matrix: White Region is Being Stretched [3]

On the other hand, when a uniaxial extensional deformation is applied to polymers that have long chain branching or a different, non-linear backbone structure, their viscosity increases at high strains/strain rates, described as an extensional thickening, or strain hardening response (Figure 4)

For the uniaxial extensional deformation, this strain hardening response occurs in the non-linear viscoelastic regime. An easy way to identify whether a polymer melt is exhibiting strain hardening behavior is by using the principle of Trouton's ratio. Trouton found that the transient extensional viscosity of a material in the linear viscoelastic regime will always be exactly three times the transient shear viscosity at the same strain rate, as seen in Equation 2 below[4].

$$\eta_E = 3 * \eta \tag{2}$$

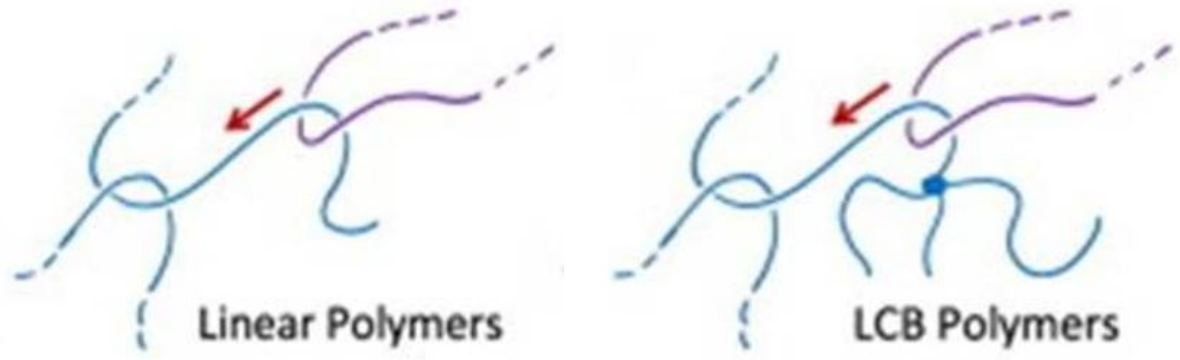

Figure 4: How Long-Chain-Branching Causes Extensional Thickening in Polymers

Because of the relative ease of testing and the versatility of the deformation mode, shear rheology (Figure 5) is utilized much more often than extensional rheology to study the flow and deformation characteristics of a material in industry.

However, certain processing conditions involve the extensional deformation of a polymer melt, including "fiber spinning, thermoforming, film blowing, blow molding, and foam production"[4], with a packaging application specifically focused on thermoforming, film blowing, and blow molding. Because film blowing is so essential in producing plastic films used every day, such as food packaging, medical films, and garbage bags[14], laboratory tests have been developed that can predict the performance of a new polymer compound in a film blowing process. Typically, there is a strong, direct correlation between a material's extent of extensional thickening (strain hardening) and its melt stability as a blown film[14],[15]. Because high molecular weight polyolefins such as polyethylene and polypropylene are often used for the development of these films, studies have been conducted that demonstrate this relationship. Münstedt et al. found that for various low density polyethylene (LDPE) compounds, the homogeneity of bubble film thickness relied on the occurrence of extensional thickening at high strains in a uniaxial deformation[15]. Kolarik et al. arrived at the same conclusion when comparing three LDPE compounds with different amounts of long-chain

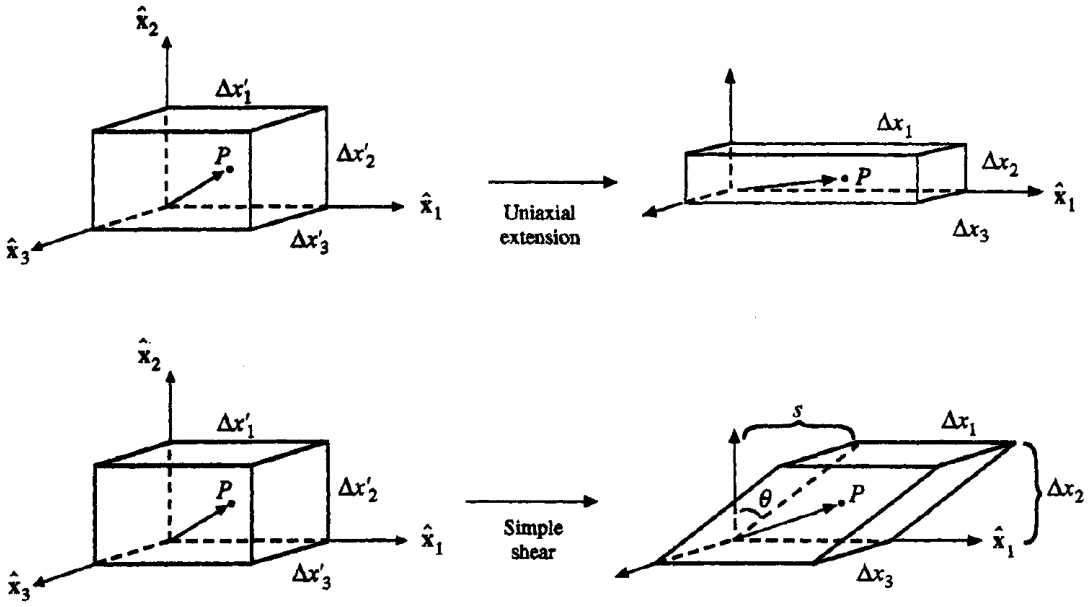

Figure 5: Deformation Motions for Shear vs Extensional Rheology [4]

branching, but extended the work by comparing to theoretical constitutive models in order to explore the relationship between a strain hardening parameter, ξ, used to control the extent of strain hardening as defined by the maximum extensional viscosity normalized by 3 times the shear viscosity in Equation 3, and both the "film blowing stability window size" and the "minimum achievable final film thickness"[14].

$$Strain\ Hardening = \frac{\eta_{E,max}}{3\eta_0} \tag{3}$$

They found from the experimental and theoretical calculations that there existed an optimal balance between bubble stability and minimum film thickness by manipulating ξ to control the degree of strain hardening, but each substantially improved over a general increase in strain hardening behavior[14]. In this thesis, the strain hardening definition shown in Equation 3 was used to quantify the extent of strain hardening in modified PHBV composites. With increased branch-like behavior, seen explicitly as an increase in crosslink density apparent through gel content measurements, the strain hardening should

increase. These modified PHBV composites could then be optimized and evaluated using extensional rheology to develop new, biodegradable compounds that can form stable and thin bubbles in a film blowing application.

2.1.3 Thermal and Physical Properties of PHBV

Because viscosity of polymers is so heavily dependent on temperature, it is essential to be aware of relevant thermal properties, such as thermal conductivity, k, specific heat capacity, C_p, the glass-transition temperature, Tg, and the melting point temperature, Tm, when characterizing a polymer's rheological behavior. A literature search was conducted to find the thermal conductivity and specific heat capacity of PHBV. No information on the thermal conductivity could be found for PHBV specifically, but the thermal conductivity of pure PHB was found to be 0.419 $\frac{W}{m*K}$, so for this thesis, it will be assumed that k for PHBV is similar to this and the value 0.419 will be used for calculations[16]. C_p was approximated to be 1250 $\frac{J}{kg*K}$ based on a graph of C_p versus temperature for pure PHBV for the purposes of simplifying a heat transfer calculation described in the results and discussion section[17]. The actual Tg and Tm of the PHBV used for testing was determined in-house using a differential scanning calorimeter (DSC), with approximate values of Tg = 5.6 °C and Tm = 172 °C[2]. These values were assumed to be similar for the other three composites tested in this thesis (see Table 2)[2].

With regards to the physical properties of PHBV, the molecular weight of the compounds that were experimented on was never measured using in-house gel permeation chromatography (GPC) or a similar technique. A typical raw PHBV has a number average molecular weight on the order of magnitude of 100000[8]. However, it should be noted that the PHBV that was used had been processed in an extruder and consequently experienced degradation by β chain scission, resulting in an abnormally low molecular weight specimen. The crystalline density of the PHBV was determined experimentally and found to be 1.25 g/cm^3, and the melt density 0.91 g/cm^3. These values were used as input parameters so

the TRIOS software on the Discovery HR-3 rheometer could appropriately calculate the transient extensional viscosity. Table 1 below summarizes the relavent thermal and physical properties that were used for PHBV and the other composites in this work.

Table 1: Summary of Relevant Thermal and Physical Properties of PHBV

Property	Value
Crystalline Density (kg/mˆ3)	1250
Melt Density (kg/mˆ3)	910
Thermal Conductivity (W/m*K)	0.419
Constant Pressure Heat Capacity (J/kg*K)	1250
Glass Transition Temperature (Tg, °C)	6
Melt Point Temperature (Tm, °C)	172

2.1.4 Application of Williams-Landel-Ferry (WLF) Equation

Time temperature superposition is a technique commonly used to understand how a polymer will behave at deformation rates or frequencies that are too high or too low to easily measure with a rheometer[18]. The temperature dependence of a polymer's viscosity is typically described by two equations. Equation 4 below is the Andrade-Eyring equation, typically used for temperatures well above any significant structural transition in the polymer, such as the Tg or Tm [4].

$$\eta = \eta_{\infty} exp(\frac{E_{\eta}}{RT}) \tag{4}$$

For temperatures closer to these transitions, the Williams-Landel-Ferry (WLF) equation is used, as shown in Equation 5.

$$log(\frac{\eta T_r \rho_r}{\eta_r T \rho}) = \frac{-C_1(T - T_r)}{C_2 + T - T_r} = log(aT) \tag{5}$$

Sources are conflicted as to the specific temperature range over which this equation should be utilized. Some references suggest it only be used between the polymer's Tg to $Tg + 100°C$ [4], while some claim the range to go to $Tg + 200°C$ [19]. This discrepancy is relevant for this thesis, as the Tg of pure PHBV is about 6°C and the testing temperatures range from 180-210°C. Despite the conflicting information, the WLF equation was still used because it is only slightly above the Tm of the material of 172°C, and it is recommended to only use the Andrade-Eyring equation for temperatures significantly above this[4].

2.2 Research Significance

The literature has demonstrated a strong connection between a material's strain hardening behavior, observed through an extensional rheological characterization of the material, and that material's melt strength when used in processing regimes involving extensional flows, such as film blowing and blow molding[14],[15]. However, these demonstrations are limited to studies on polyolefins with relatively high viscosities and molecular weights that are derived from petroleum. In the pursuit of more global sustainability through the production of biodegradable plastics and a deviation from a reliance on petroleum, it is necessary to show this connection of rheological characterization to processing performance of new, innovative bio-derived plastics, such as PHBV. This research presents a method that overcomes the challenges of performing this characterization with lower molecular weight/lower viscosity materials, and successfully predicts the structural modification of the tested polymer composites. As this modification, including increasing long-chain branching and/or crosslink density, has shown a strong connection to processing performance, this research is an important and necessary stepping stone to evaluating the potential of new bio-derived materials in film blowing and blow molding applications.

2.3 Overview of Thesis

The introduction section presents the concepts necessary to understand the rheological discussions present throughout the thesis as well as the background and justification for the assumptions made to perform analytical calculations in the results section. The experimental methodology section outlines the refined method developed to overcome the adversity associated with studying the extensional rheology of PHBV, as well as the shear methods used to supplement the analysis of the extensional data in the results section. The results and discussion section presents the steps taken to transform the data into something presentable, including using a lumped system analysis to approximate sample temperature, using the WLF equation to shift all sample temperatures to the same reference temperature, and comparing the shifted extensional data to transient shear data to evaluate the accuracy of the extensional results as well as the degree of strain hardening for each compound. Some of the equipment is shown in the Appendix, and a notation guide is included to explain the meaning of variables and abbreviations.

3 Experimental Methodology

For all of the testing completed for this thesis, PHBV compounds developed by Zhao et al. were used, with the basic sample differences denoted in Table 2 below[5].

Table 2: Composition of Compounds Used for All Testing[5]

Label	**Natural Rubber Loading (wt%)**	**Peroxide Loading (PHR)**	**Coagent Loading (PHR)**
PURE	0	0	0
15NR	15	0	0
PEROX	15	3	0
COA	15	3	4.2

To simplify the discussion and presentation of the results, the abbreviations specified in the Label column in Table 2 will be used to refer to the different compounds throughout.

3.1 Dynamic and Transient Shear Rheology

Dynamic shear testing was conducted for each of the 4 compounds to assist with the data processing of the extensional rheology testing. Specifically, dynamic shear data was used to evaluate the degradation behavior of these 4 compounds, as well as to find temperature shift factors to be applied to the extensional data. Lastly, the transient shear rheology testing was conducted to provide a comparison to the transient extensional results relating to the Trouton ratio.

3.1.1 Apparatus and Sample Preparation

For the dynamic shear testing, a Discovery HR-3 rheometer by TA Instruments (New Castle, DE, USA) was used. The 25mm parallel plate geometry has a fixed bottom with a mounted platinum resistance thermometer (PRT) right below the bottom stainless steel

plate. Because of this mounting location, the temperature control for the shear testing on this rheometer is more reliable than the PRTs on the walls of the oven that are used in the extensional fixture setup. Additionally, as the bottom plate is mounted, the motor and transducer are on the same side of the sample. Consequently, the motor's behavior is related to the transducer reading by a feedback loop control scheme and thus is unable to function independently. As a result, a transient shear test cannot be done using this stress-controlled rheometer, as it takes too long for the motor to reach the desired constant shear rate while deforming the sample. Instead, an ARES LS2 rheometer (New Castle, DE, USA) was used, which has the motor connected to the bottom plate while the transducer measures the response of the top, allowing the motor to behave independently.

Samples were prepared through compression molding of the compounds in 25mm disk molds to a thickness of approximately 1mm. Similar to the compression molding used for the extensional sample preparation, the set-point temperature was 190°C to expedite the melting process.

3.1.2 Dynamic Shear Testing for Compound Degradation

PHBV has a polyester backbone and consequently degrades by β elimination at high temperatures. Due to the limited quantity of the PEROX and COA samples for testing, only the degradation behavior of the PURE and 15NR compounds were evaluated. First, a strain sweep was conducted to ensure the peak oscillation strain for the dynamic testing was within the linear viscoelastic regime. From this and previous experience, a strain of 0.3% was selected for the dynamic shear testing. To evaluate the degradation behavior over time, samples were deformed to 0.3% strain at 1 Hz for 100 seconds at a constant temperature, using the Discovery HR-3 rheometer. This was repeated for the temperatures of 180, 190, 200, and 210°C.

3.1.3 Dynamic Shear Testing for Time-Temperature Superposition

Because of the general inability to measure sample temperature in extensional experiments, dynamic shear testing was conducted to determine shift factors that could be applied to extensional data to allow the data to be presented at approximately the same temperature. For each of the four compounds, a frequency sweep was conducted from 100 to $1s^{-1}$ at an oscillation strain of 1% and at a constant temperature, using the Discovery HR-3 rheometer. This was repeated for the temperatures of 180, 190, and 200°C. The frequency sweep was conducted from high frequency to low frequency because of the known presence of the degradation phenomenon at high temperatures. By testing in reverse order, since the higher frequencies take less time to measure, more data could be collected before significant degradation occurred. The selected oscillation strain of 1% was selected because it was within in the linear viscoelastic regime.

3.1.4 Transient Shear Testing to Compare with Transient Extensional Testing

Because of the inability of the Discovery HR-3 rheometer's motor to act independently of the transducer, an ARES-LS2 rheometer was used for this testing instead. Samples were pre-heated to a constant temperature and a constant strain rate was stepped to for a duration of 60 seconds. This was repeated for strain rates of 10, 5, and $3s^{-1}$, as well as temperatures of 180, 190, and 200°C.

3.2 Transient Extensional Rheology

3.2.1 Apparatus and Sample Preparation

To complete all of the extensional rheology testing, the same instrument, the Discovery HR-3 rheometer, was used. This rheometer features an extensional attachment, Sentmanat Extension Rheometer (SER3), with two rotating drums that are suspended in air. The air is heated by a forced convection oven and the temperature of the air is measured using

two platinum resistance thermometers mounted on the interior of the oven. Figure 23 in the Appendix shows the extensional attachment installed with the oven open. Samples for this testing regime were prepared using a mold provided by TA Instruments and a melt press at 190°C. The temperature well above the melting point of PHBV was selected to expedite the molding process, but residence times in the mold were minimized to mitigate potential for sample degradation by β elimination at the high temperature. Once removed and cut from the mold, each sample was cut lengthwise to be approximately 15mm long to avoid the sample hitting itself at high strains. Additionally, the width and thickness of each were measured using a dial caliper and recorded for future calculations. The sample width was relatively constant at about 10mm, but the thickness varied drastically from 0.7mm to 1.2mm.

3.2.2 Procedure Development

The Discovery HR-3 rheometer's SER3 fixture is designed for polymers that have a high viscosity even in the melt state. For example, typical petroleum-derived thermoplastics such as polyethylene are usually polymerized to have molecular weights on the order of 10^5 to 10^6 repeat units, resulting in a relatively high viscosity. The PHBV compounds of interest on the other hand have molecular weights on the order of 10^3 to 10^4 repeat units, about two orders of magnitude lower than what the fixture was designed for. Consequently, issues were encountered when attempting to measure the extensional viscosity over time for these PHBV compounds.

With the goal of measuring the transient extensional viscosity at varying uniaxial extension rates, an appropriate test was developed using the TRIOS software provided with the TA rheometer. When attempting to run a test as instructed by the TA help manual for the instrument, the issues associated with using a brittle, relatively low melt viscosity compound like PHBV became apparent. Figure 24 in the Appendix shows the setup for the test, specifically how the sample is placed onto the drums. In order for the sample

to stick, it needs to either be very tacky to begin or melt and consequently experience an increase in its tackiness. The normal procedure would be to slide the sample into guiding clips that are attached to the drums preheated above the melting point of the compound, close the oven, and allow the sample to equilibrate to reach the desired temperature and uniformly melt. However, because of the low viscosity of PHBV, gravity causes the center of the sample to be pulled down and exhibit a sagging phenomenon in a relatively short amount of time (5-10 seconds after melting). Additionally, the brittle mechanical nature of PHBV at room temperature prevents it from being easily wrapped around the drums and melted. To overcome these kinetic issues, the preheat temperature of the drums was substantially increased to 240°C and the set point temperature during the stretching period was left at 240°C to allow the sample to melt as fast as possible. Additionally, all pre-stretch steps were eliminated, as they only added more inconsistency to the testing due to the low viscosity of the samples.

A related issue was knowing when the sample melted in the first place. Working with a closed oven without a camera, it was impossible to know exactly when the sample had completely and uniformly melted before testing began. To overcome this, the soak time before the test began was determined iteratively using a stopwatch and checking whether the sample had melted at different elapsed times. To approximate the true sample temperature at this time and during the time of testing, a simplified heat transfer calculation was conducted, discussed further in the results and discussion section. Finally, because the Discovery HR-3 rheometer is stress controlled, the motor is not able to achieve the constant stretching rate instantaneously. Rather, it relies on a control feedback loop between the transducer and the motor to work its way up to the set point stretching rate. However, because of the relatively low viscosity of the sample, this still happens in about 0.2 seconds, so the associated error from this phenomenon only affects the very early buildup of extensional viscosity, discussed more in the results and discussion section.

3.2.3 Final Procedure

Using the knowledge obtained in the procedure development section, the final procedure was decided. For each sample, the drums were pre-heated in the oven to 240°C, allowing for a long equilibration time (15min) when first heating the drums to ensure they reached the desired temperature. Meanwhile, the sample dimensions were measured and entered into the testing software to be used for the calculation of the constant volume of the sample. The sample was then placed on the drums and allowed to melt at the contact points by applying pressure with one's hand. Once affixed to the drums, the oven was quickly closed and the test quickly started, with about 1 second separating the time of closing the oven to the time of the test beginning. The test procedure began with a 15 second soak time for the sample. Then, the sample was stretched uniaxially at a constant stretching rate of either 1, 3, 5, 8, or $10s^{-1}$ to a strain of 3.4, the maximum achievable strain before the sample collides with itself. Immediately after the test, the oven is opened to observe the final state of the sample. The test is considered legitimate only if the stretching appeared to be uniaxial, uniform, and without significant sagging occurring, as seen in Figure 25 in the Appendix. Additionally, only tests where the measured data was not full of errors was used. This was determined by viewing the data for the torque measurement from the transducer. For the Discovery HR-3 Rheometer, the torque transducer limit is 100 µN*m, so if a significant portion of the test gave a measurement below this limit, it was considered illegitimate. Finally, the observed behavior had to be generally repeatable, so the same behavior had to be observed at least twice along with passing the other requirements for a test to be considered legitimate.

4 Results and Discussion

4.1 Shear Rheology

4.1.1 Dynamic Shear Testing for Compound Degradation

Because of the known degradation of PHBV by β elimination of the ester backbone at high temperatures[8], an exploration into the compound's breakdown over time was necessary to ensure that the testing could be done in a way that would mitigate the influence of this phenomenon, and to understand how it would affect the interpretation of the results. Dynamic shear testing was conducted to see how the complex viscosity of the PHBV changed over time at a constant high temperature. To remove the potential influence of non-linear viscoelastic behavior in this analysis, a strain sweep was first conducted for the PHBV and the COA compounds to better understand the linear viscoelastic region. These two particular compounds were selected because they represent the extremes in the design space for the four compounds: if these two compounds were both in the linear regime at a certain strain, it was safe to assume the other two would be as well. The results from the strain sweep are shown in Figure 6 below.

As seen in Figure 6, up until about 12% strain, the complex viscosity remains approximately constant, so any strain less than this is within the linear viscoelastic regime. Unfortunately, by mistake, the strain sweep was conducted at a frequency of 1.59 Hz, while the degradation testing used a frequency of 1 Hz. Theoretically, decreasing the frequency should put the degradation testing even more in the linear regime within the same strain range, but it should be noted that the frequencies are not the same. For the degradation testing, a strain of 0.3% was used to remain well within this linear region. The degradation testing was conducted only for two of the four compounds, the PURE PHBV and the 15NR, because at the time there was concern regarding the amount of the other two materials remaining for testing. A time sweep was conducted at 1 Hz to 0.3% strain for

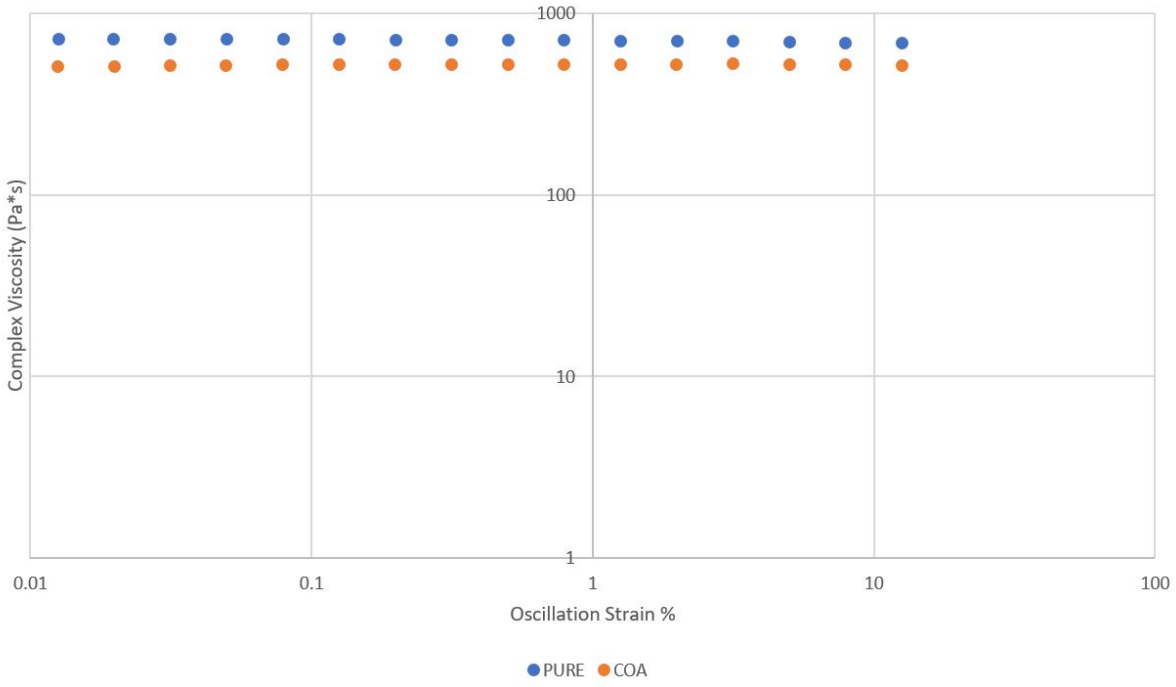

Figure 6: Oscillation Strain Sweep: Linear Viscoelastic Regime: 180°C, 1.59 Hz

100 seconds for these two materials, and repeated for the temperatures of 180, 190, 200, and 210°C. Figure 7 below shows the results of the degradation testing.

As seen in Figure 7, as temperature increases, the rate of degradation also increases, with the viscosity decreasing more rapidly in the samples at higher constant temperatures. Additionally, while the 15NR compounds have a lower initial viscosity than the PURE compounds, they have a lower slope over time. While PHBV degrades primarily by β elimination, NR is susceptible to thermo-oxidative chain scission, a process accelerated by high stresses/strains on the compound. In this particular experiment, the stresses are relatively low, so the rate of NR chain scission may be lower than the rate of β elimination of the PHBV, resulting in a compound that is stable relative to pure PHBV. Additionally, because the NR chains are so much longer than those of PHBV, the scission of a chain may have an overall lower effect on the complex viscosity, as the remaining two chains are still relatively large.

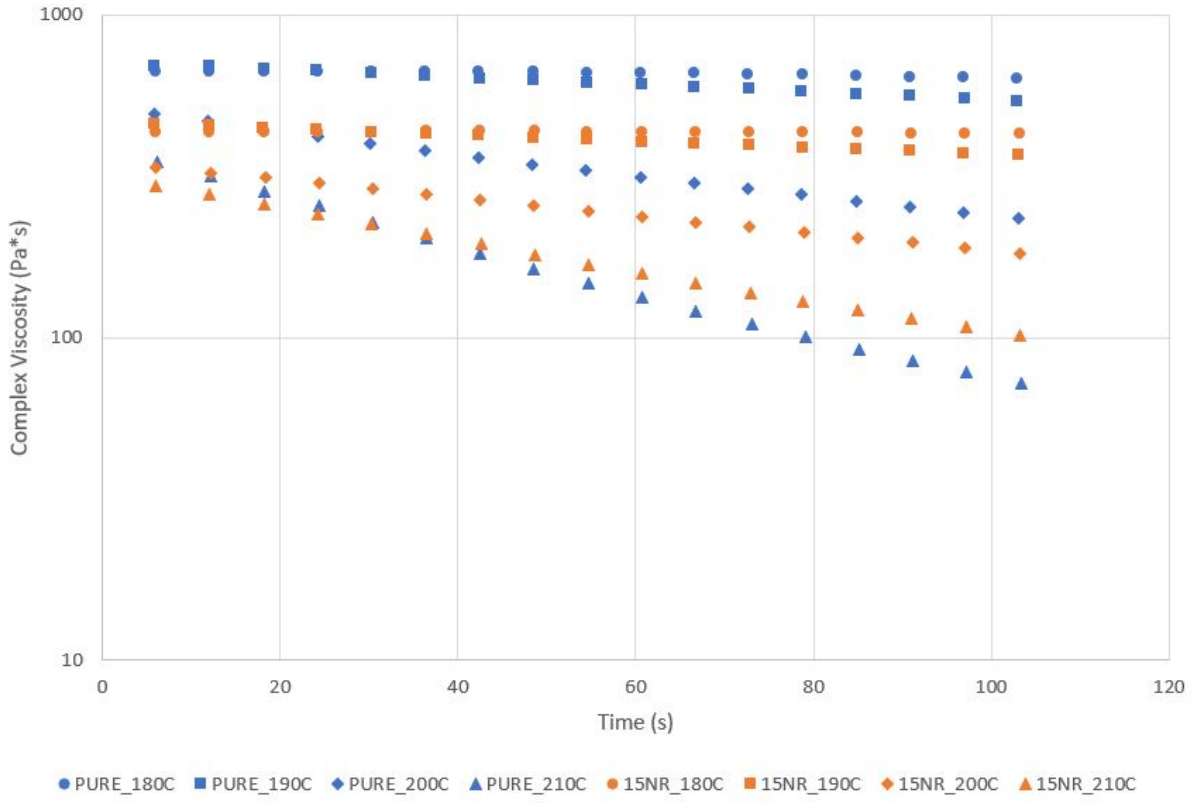

Figure 7: Oscillation Time Sweep: Observing Degradation Behavior: 1Hz, 0.3% Strain

The important takeaway from the degradation testing for the purposes of this study was that at short times, even at high temperatures, the change in viscosity was negligible. The transient extensional viscosity testing heats the sample for 15 seconds before testing for about 1 second, giving a total test time less than 20 seconds. Comparing this to Figure 7, assuming the sample only reaches these high temperatures for the last few seconds of the test, no signifcant degradation should occur. However, for the dynamic shear testing to find shift factors, the total testing time was approximately 250 seconds. As a result, significant degradation occurred by the end of the frequency sweeps, and the results had to be truncated accordingly, as detailed further in the next section.

4.1.2 Dynamic Shear Testing for Time-Temperature Superposition

Because the sample temperature could not be exactly measured in the transient extensional testing, the temperature had to be approximated using a basic heat transfer model, detailed further in the transient extensional viscosity section. When applying this model, it was found that for the same testing method, each compound was reaching a drastically different final temperature. Because temperature has such a significant impact on viscosity, it was impossible to accurately identify trends in this data if left unmodified. In order to meaningfully present the viscosity data from the transient extensional testing, shift factors were determined using dynamic shear testing so the extensional data could all be shifted to the same reference temperature. The Williams-Landel-Ferry equation for time-temperature superposition, seen in Equation 5[4], was used, with section 2.1.4 detailing the validity of the application of this equation to this polymer system.

To obtain data to use for this equation, a frequency sweep was conducted from 100-1 Hz at 3 different temperatures: 180, 190, and 200°C. The higher frequencies were tested first to allow as much data as possible to be obtained before significant degradation occurred. In a typical frequency sweep, the zero-shear viscosity should be approached as the frequency is decreased[4]. However, because of the degradation phenomenon, the complex viscosity decreased after reaching a peak as frequency decreased. This behavior was most significant for the PURE compound because the blends are less susceptible to degradation, as seen in Figure 8.

Because this was a result of the degradation, the data after the viscosity peaked at lower frequencies was truncated before further analysis. The trends in Figure 8 provide more evidence of the blends' resistance to degradation relative to the pure PHBV, confirming that both the PEROX and COA compounds, which did not have formal degradation testing on them prior, do show comparable, if not increased, resilience relative to the 15NR compound.

Using the truncated data for each compound, the WLF shift factors, aT, for each tem-

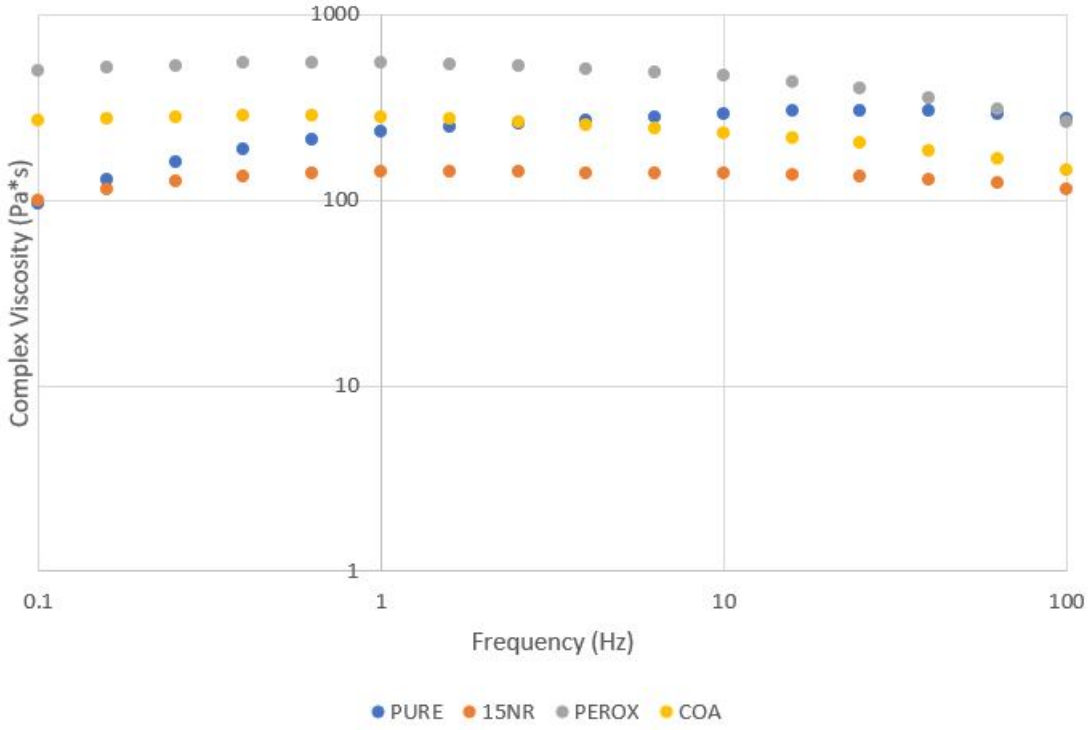

Figure 8: Error with Dynamic Data Caused by Degradation: 200°C, 0.3% Strain

perature were found by plotting the G' and G" results for each temperature and adjusting the aT for each temperature until the curves aligned[18]. Once aligned, the aT values for each temperature were used to fit the WLF constants C_1 and C_2 to the data for each particular compound. Due to the error from degradation in the testing, only 1 of the 4 compounds were able to be successfully fit to the WLF equation. Figure 9 below shows the manually shifted dynamic data for the PEROX compound. Figure 10 shows the WLF equation fit to the 3 shift factors derived for this compound.

Because the 4 compounds largely have the same polymer backbone structure, and due to a lack of comprehensive data, an approximation was made to assume that the shift factors found for the PEROX compound could be applied to the other 3 compounds as well. Thus, in the data shifts for the transient extensional viscosity, the WLF equation was applied using the fit constants of $C_1 = 4.09$ and $C_2 = 125.96$.

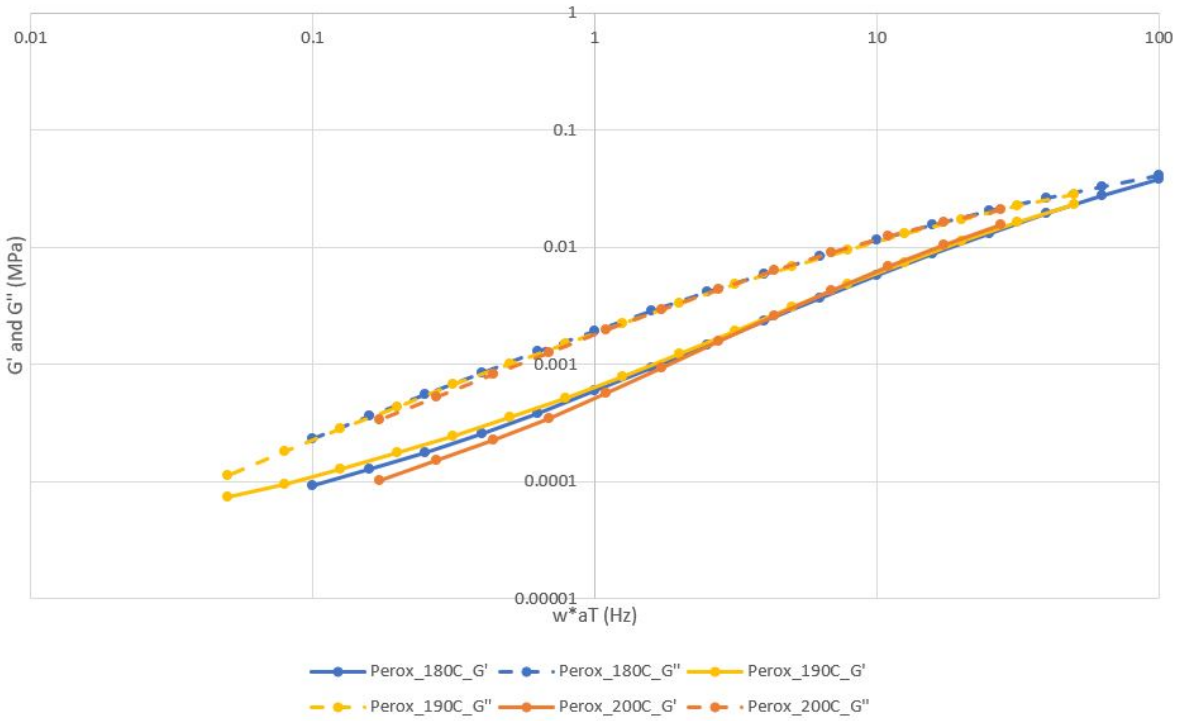

Figure 9: PEROX G' and G" Frequency Sweep: Shifted to Find aT Values: 180°C

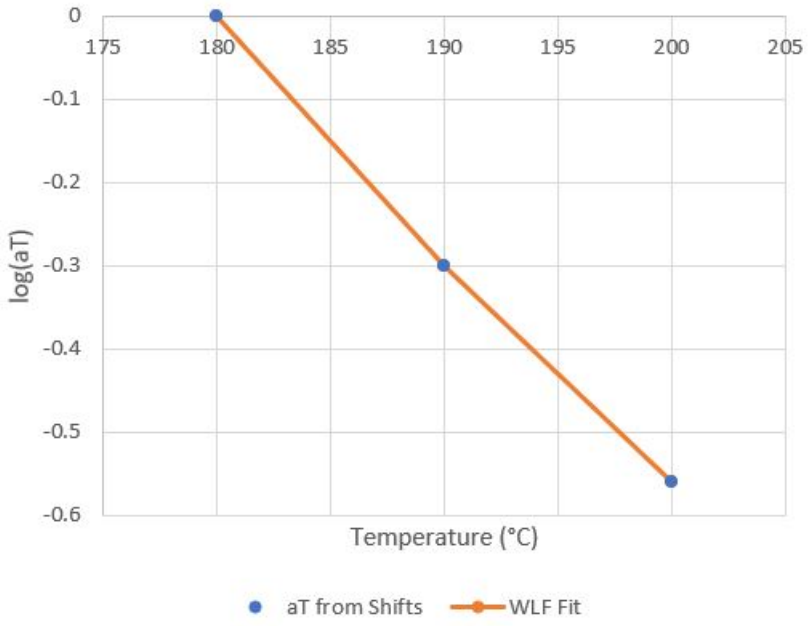

Figure 10: WLF Fit to aT Values Derived from Manual Shift: PEROX

4.1.3 Transient Shear Rheology

A good way to validate transient extensional data is to compare it with transient shear data. To provide a data set to compare to the transient extensional data, transient shear testing was done at the same rates as the extensional testing. Due to limitations in the Discovery HR-3 rheometer, detailed further in the methodology section, an ARES-LS2 rheometer was used to collect this data. For each of the four compounds, transient shear data was collected for 60 seconds at a constant temperature, 180°C, later to be used as the reference temperature for shifting the extensional data. Figure 11 summarizes the results for the data collected at 180°C. When collecting this data, a significant mistake was made regarding the setup of the rheometer, where the geometry of the parallel plate used had a diameter of 25mm, but the data acquisition software was instructed to perform the test as if the diameter were 50mm. From the working equations on parallel plate geometries reported by Macosko[4], it was determined that the calculation could be retroactively adjusted by multiplying the transient viscosity data by a factor of 16.

The presence of local maxima at short times seen in the shear viscosity as a function of time in Figure 11 suggests that stress overshoot, a sign of non-linear viscoelastic behavior, was present at short times. However, because the transient extensional viscosity data was unobtainable at short times with the Discovery HR-3 rheometer, this non-linear behavior seen in the shear regime does not have anything to be compared to for the purpose of understanding the extensional data. Ideally, this stress overshoot at short times should be avoided but in this instance may be attributed to slip at the boundaries of the sample between the parallel plates, causing a local maximum at short times. At long times however, the stress overshoot likely is non-linear viscoelastic behavior, an unexpected result for the relatively low shear rates tested. However, because only the steady-shear viscosity was used to compare to the extensional data directly and each data set appeared to have approximately reached steady state, the presence of the non-linear behavior does not affect

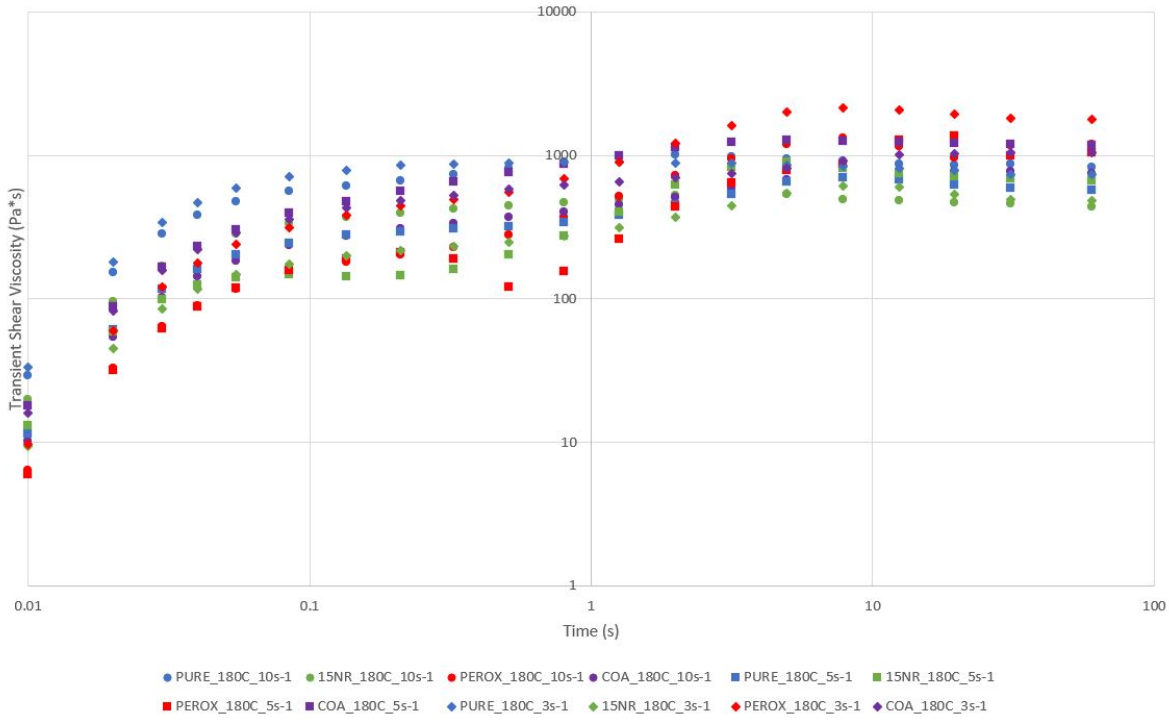

Figure 11: Transient Shear Data from ARES LS2 at 180°C

the methods for comparing the two flow regimes presented in this thesis.

Although there is some variation in the viscosity data for each compound at different shear rates, when comparing each of the compounds' averages to one another, a clear trend is present. The PEROX compound has the highest steady-shear viscosity, followed by (descending) COA, PURE, and 15NR has the lowest steady-shear viscosity. As seen in the extensional rheology section, at higher extension rates, the COA compound has a significantly higher extensional viscosity at longer times than the PEROX compound. This is an important distinction, while the PEROX shear viscosity at the same rate is higher than the COA, the COA has the higher extensional viscosity at higher rates due to a more significant non-linear, extensional thickening behavior. There is no strong correlation between shear and extensional rheology data in the non-linear viscoelastic regime[4].

4.2 Transient Extensional Rheology

4.2.1 Approximating Actual Sample Temperature

The Sentmanat Extension Rheometer (SER3) attachment used with the Discovery HR-3 rheometer is limited by its inability to directly measure the sample temperature during a test. Platinum resistance thermometers are mounted on the walls of the oven interior to measure the air temperature, but the low thermal conductivity of most polymer samples means a typical sample would require time to equilibrate to reach exactly the measured air temperature. Because PHBV is a relatively low viscosity polymer in the melt state, this equilibration time is not possible, as gravity deforms the sample until failure once it has melted. Because the sample could not equilibrate, an alternative method of approximating sample temperature was used. The first significant assumption made was that the heat conduction was negligible to the temperature of the part of the sample that would be deformed. Because PHBV has such a low thermal conductivity, approximately 0.419 $\frac{W}{m*K}$, it was assumed that the center of the sample that was not touching the barrels would heat an insignificant amount before the oven was closed. After closing the oven, it was assumed that the only heat transfer mechanism to the sample was by convection from the hot air. A lumped system analysis was used to simplify the heat transfer modeling by treating the temperature of the center of the sample as uniform. In order to make this assumption, the Biot number, defined in Equation 6, should be less than 0.1[20].

$$Bi = \frac{hL}{k} \tag{6}$$

The characteristic length of the samples, L, was defined as the thickness. The thermal conductivity, k, was assumed to be 0.419 $\frac{W}{m*K}$ for all compounds. The convective heat transfer coefficient, h, was calculated using an empirical equation for air velocities between 2 and 20 m/s, seen in Equation 7 below, where h has units of $\frac{W}{m^2*K}$ [21].

$$h = 12.12 - 1.16v + 11.6v^{1/2} \tag{7}$$

The air velocity was approximated based on the diameter of the tube feeding the air to the forced convection oven and the set volumetric flow rate on the flow meter: 15 L/min. For the range of thicknesses of samples used for testing, the biot number ranged from 0.050 to 0.085. Because the biot number is less than 0.1, a lumped system analysis can be safely applied to this process. The governing equations for the lumped system analysis are shown in Equations 8 and 9 below.

$$\frac{T(t) - T_\infty}{T_i - T_\infty} = exp(-bt) \tag{8}$$

$$b = \frac{hA}{\rho V C_p} \tag{9}$$

In Equation 9, b is a constant calculated from the convective heat transfer coefficient, h, the sample surface area, A, the sample density, ρ, the sample volume, V, and the material heat capacity, C_p, that is used as an exponential decay parameter in Equation 8. In Equation 8, the sample temperature as a function of time, $T(t)$, is calculated using the oven temperature, T_∞, and the initial sample temperature, Ti. For all of the calculations, Ti was assumed to have a value of 22°C and T_∞ was the oven temperature at a defined step time. By running experiments where the temperature of the oven was tracked while the sample was pre-heating, values for T_∞ were gathered over time and used sequentially to model how $T(t)$ changed over time, essentially using Equation 8 over and over to represent each sequence of elapsed time for which a new value of T_∞ was recorded. By following this method, sample temperatures at the start of testing were calculated for each test retroactively, varying greatly (180-210°C) due to the inconsistency of the sample thickness.

4.2.2 Shifting Transient Extensional Viscosity Data to one Temperature

Using the calculated temperature for each sample, its transient extensional viscosity data was shifted both vertically and horizontally to a reference temperature of 180°C. The vertical shift factor involved adjusting the viscosity based on the ratio of temperatures and the shift factor constants $C1$ and $C2$ determined in the dynamic shear data analysis, shown in Equation 10 below.

$$log(\frac{\eta T_r \rho_r}{\eta_r T \rho}) = \frac{-C_1(T - T_r)}{C_2 + T - T_r} \tag{10}$$

The densities, ρ and ρ_r, were assumed to be the same. η_r was calculated for each compound based on the calculated sample temperature, T, the reference temperature, T_r, and the extensional viscosity, η. Then, the horizontal shift factor was applied by finding aT for each sample based on the temperature calculated from the lumped system analysis and the previously determined constants $C1$ and $C2$. The horizontal shift was applied by dividing the step time, t, by the shift factor, aT, to account for the change in relaxation behavior for the polymer melts at different temperatures.

Finally, to potentially interpolate and extrapolate shifted viscosity data for each compound, the Oldroyd-B non-linear constitutive model, shown in Equation 11, was applied to each group of data sets for each individual compound.[4].

$$\tau + \lambda_1 \overset{\triangledown}{\tau} = 2\eta(D + \lambda_2 \overset{\triangledown}{D}) \tag{11}$$

The three parameters were fit to each data set by changing them to minimize the sum of residuals squared when compared to the shifted viscosity data. The results of the fitting are shown in Table 3.

All three parameters were fit to be on the same order of magnitude so as to represent approximately the same zero shear viscosity, relaxation, and retardation times (η, λ_1, and λ_2 respectively). No obvious correlation seems to be present with regards to the value of

Table 3: Oldroyd-B Model Parameters for each Sample

Compound	eta0	lambda1	lambda2
COA	2277.27	0.092	0.033
PEROX	3362.34	0.076	0.048
15NR	2012.94	0.085	0.047
PURE	2025.13	0.074	0.049

the each parameter as a function of the gel content of each compound.

Figures 12, 13, and 14 show the shifted extensional viscosity data as well as the Oldroyd-B fit for each of the compounds at extension rates of 10, 5, and 3 Hz respectively. The data was cropped based on the transducer torque limits: any data that did not register a torque of at least $100\mu N * m$ was discarded. Additionally, any data that showed very high elongational viscosity at very low elapsed times was discarded. This high viscosity data is attributed to the inertial effects of trying to immediately rotate 2 drums very quickly. Additionally, it should be noted that because of the design of the Discovery HR-3 rheometer, the extension rate could not be immediately reached, so much of the transient viscosity data at early times (t<0.25 seconds) was unattainable.

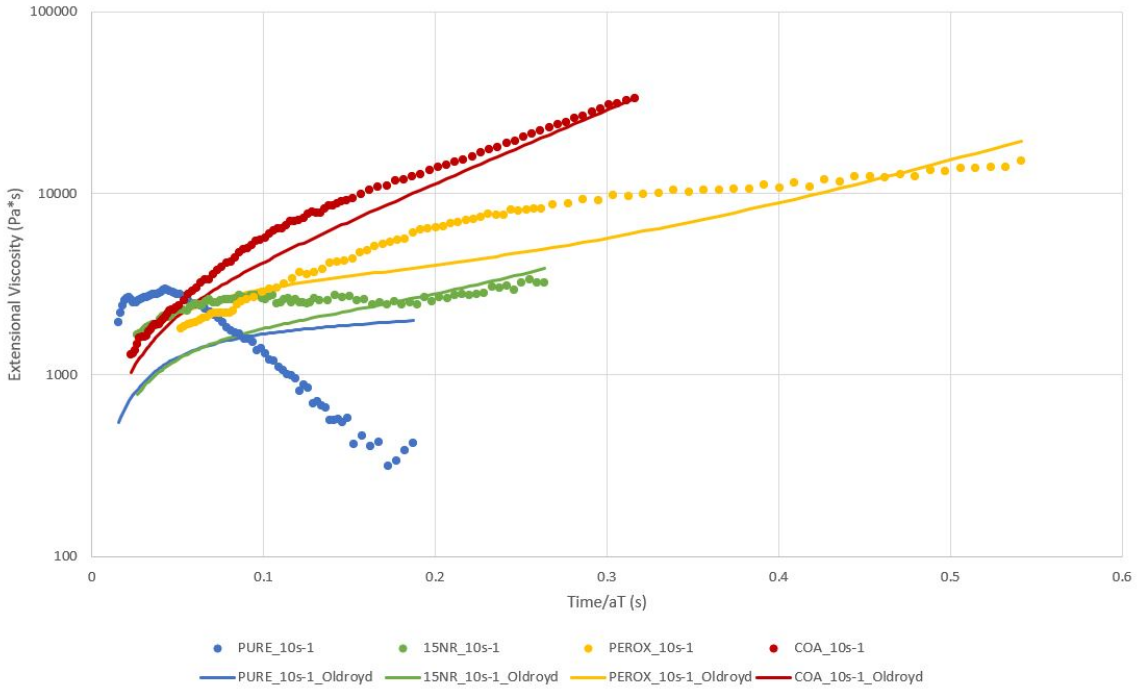

Figure 12: Shifted Transient Extensional Viscosity with Oldroyd-B Fit: 10s-1, 180°C

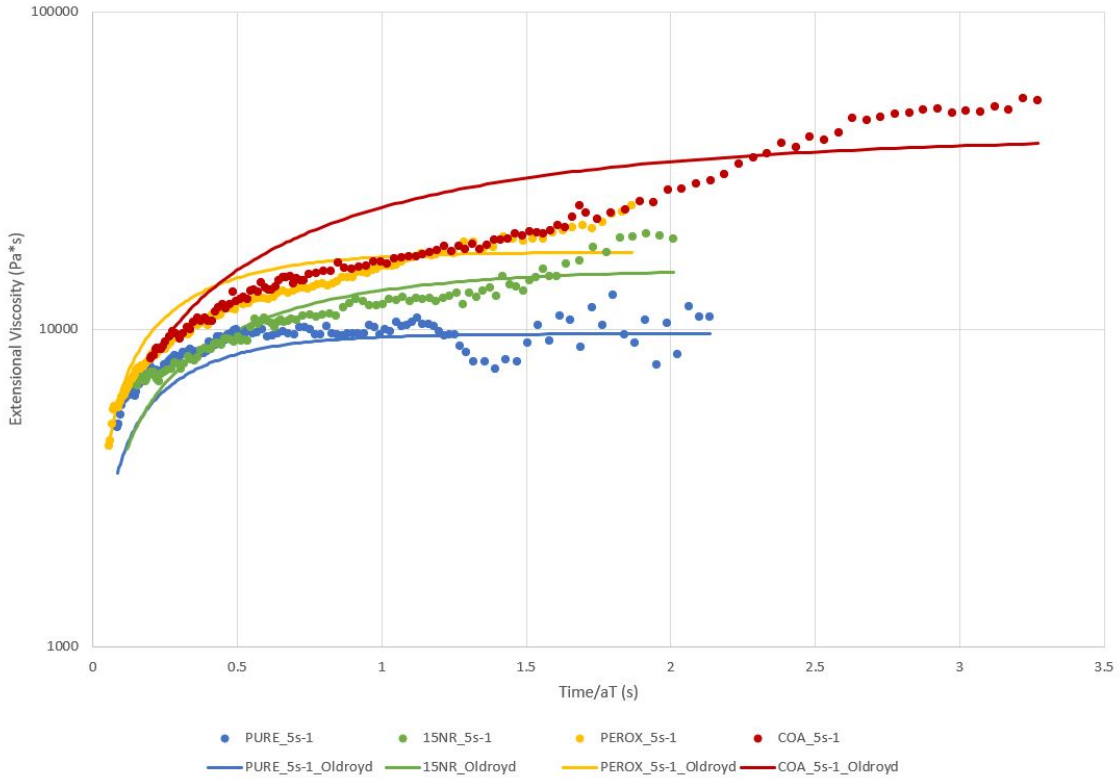

Figure 13: Shifted Transient Extensional Viscosity with Oldroyd-B Fit: 5s-1, 180°C

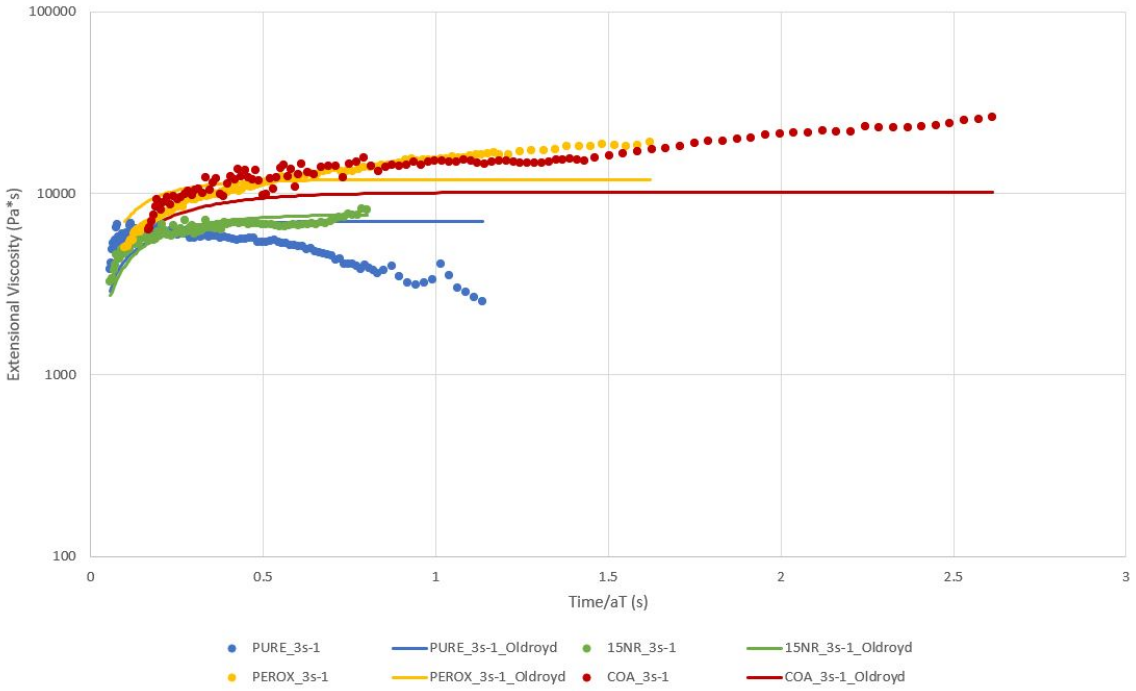

Figure 14: Shifted Transient Extensional Viscosity with Oldroyd-B Fit: 3s-1, 180°C

As seen in Figures 12, 13, and 14, as the expected degree of higher order structure, or branch-like behavior, increased, the amount of strain hardening at higher strains (longer times) increased as well. This observation aligned with what was expected based on the literature review, which showed the COA compound having a significantly higher gel content, and consequently crosslink density, than the other compounds[2]. As the extension rate decreases, the degree of strain hardening also decreases. At lower extension rates, the polymer will be less outside of the linear viscoelastic region, so the differences in strain hardening are far less noticable. For example, in Figure 14, at a rate of 3s-1, the PEROX and COA compounds behave almost identically. The pure PHBV exhibits a shear thinning behavior, weakening as it is stretched, further demonstrating the need to improve its melt strength if it is to be used in film blowing or blow molding applications.

Figures 15, 16, 17, and 18 show the same data but displayed differently, with each graph displaying the different extension rates while maintaining the same compound of PURE, 15NR, PEROX, and COA respectively.

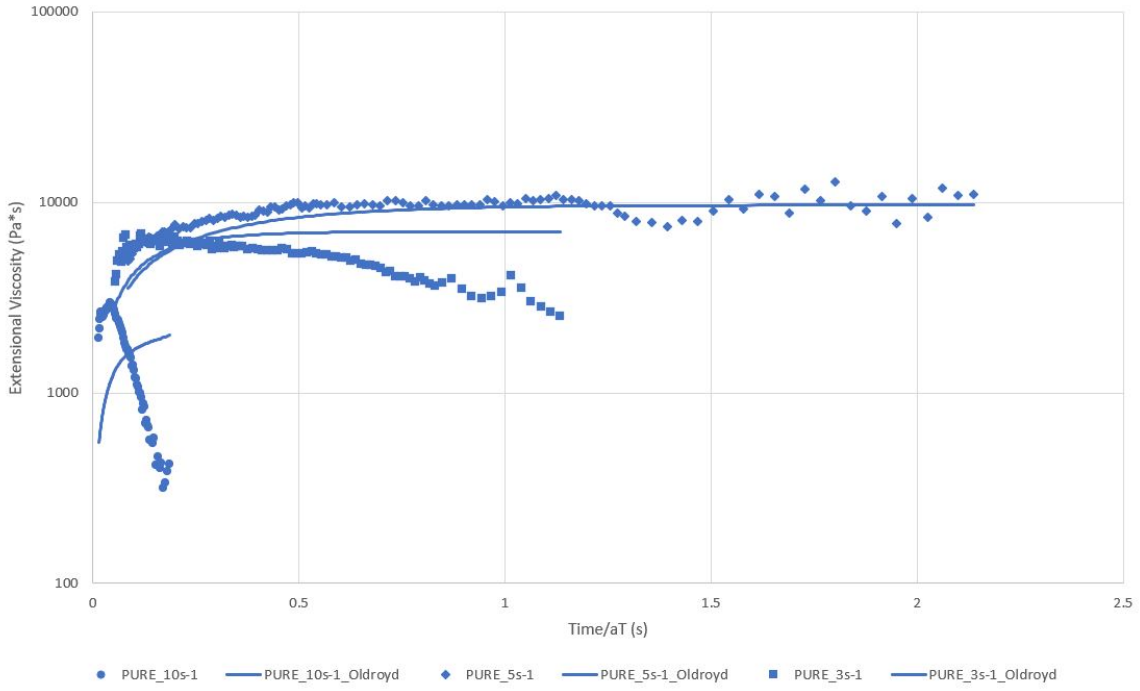

Figure 15: Shifted Transient Extensional Viscosity with Oldroyd-B Fit: PHBV, 180°C

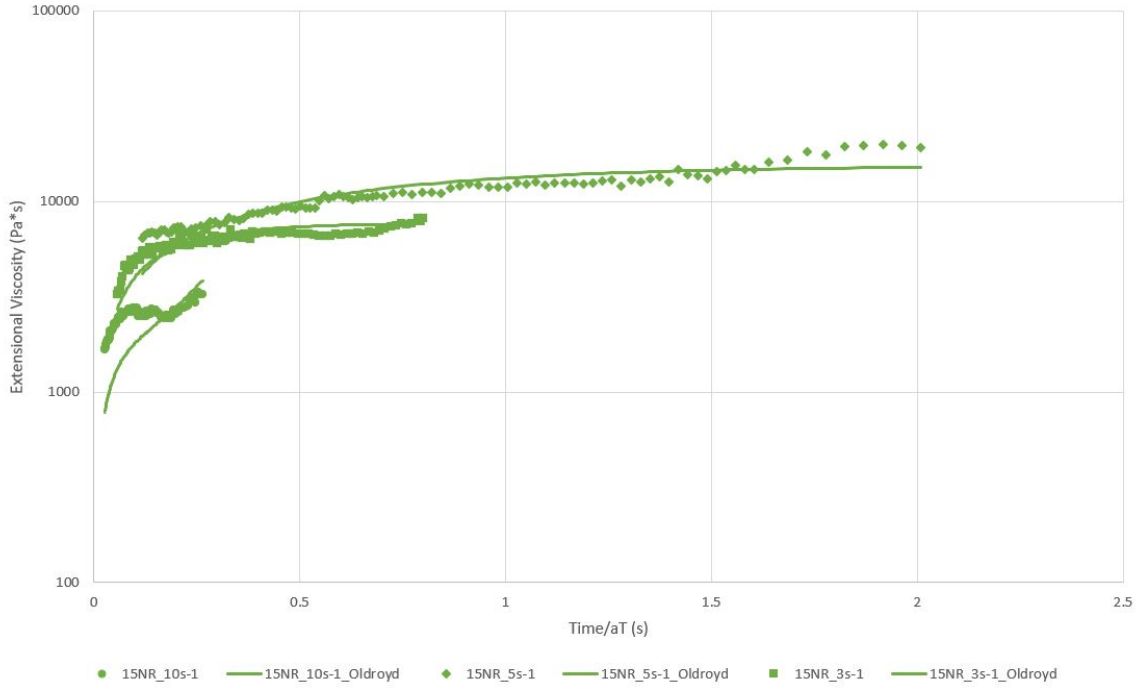

Figure 16: Shifted Transient Extensional Viscosity with Oldroyd-B Fit: 15NR, 180°C

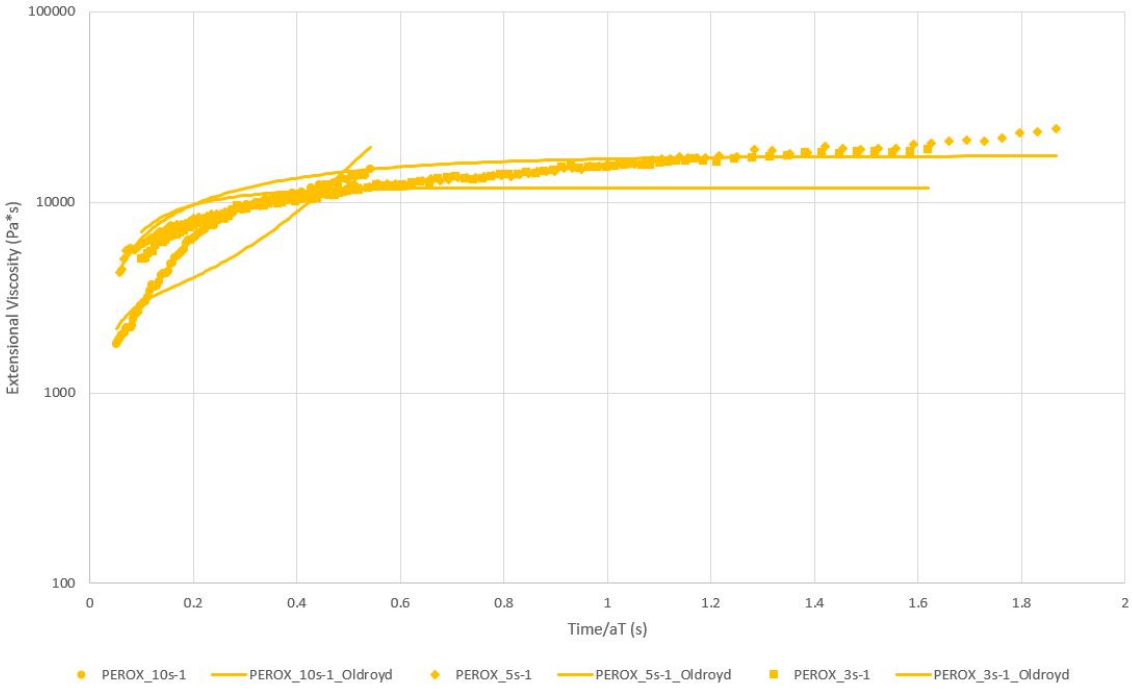

Figure 17: Shifted Transient Extensional Viscosity with Oldroyd-B Fit: PEROX, 180°C

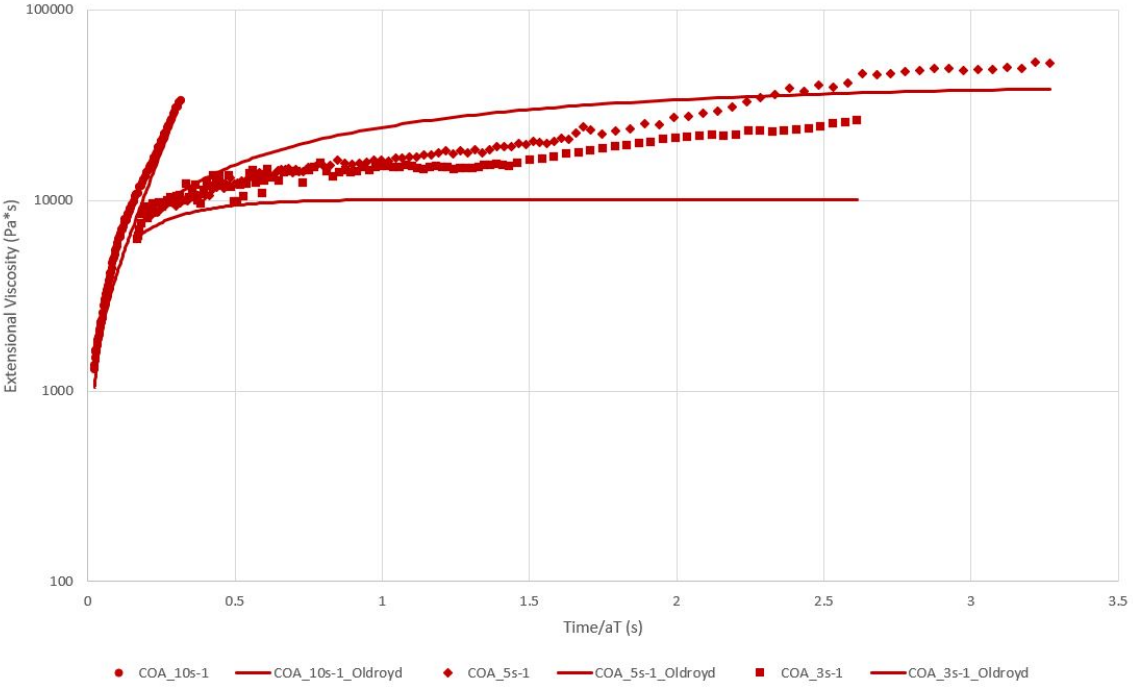

Figure 18: Shifted Transient Extensional Viscosity with Oldroyd-B Fit: COA, 180°C

When comparing the results for the COA in Figure 18 to the rest of the compounds, the slope of the highest extension rate, 10s-1, is significantly higher when compared to the other extension rates for the same compound. This suggests that increasing the extension rate would lead to an even higher strain hardening behavior in the COA compound. This trend is true for the 15NR and PEROX compounds as well, but the difference in slopes suggests that the COA has more potential for growth.

With regards to the fit of the Oldroyd-B constitutive equation, the model seemed to be unable to predict the extensional thinning behavior observed in the PURE PHBV at higher extension rates. Additionally, while the fit overall seemed to be better at short times, this was especially the case for the lower extension rates, specifically at 3s-1. As the extensional flow approaches steady-state, the Oldroyd-B expression for extensional viscosity reduces down to Equation 12 below.

$$\eta_{EXT} = \frac{2\eta_0 - 4\eta_0\lambda_2\dot{\epsilon}}{1 - 2\lambda_1\dot{\epsilon}} + \frac{\eta_0 + \eta_0\lambda_2\dot{\epsilon}}{1 + \lambda_1\dot{\epsilon}} \tag{12}$$

In Equation 12, as the extension rate, $\dot{\epsilon}$, approaches 0, the value of the extensional viscosity approaches a constant equal to $3\eta_0$. This trend can be seen at the longer times in the lower extension rate graphs, most notably for 3s-1. The model is unable to predict the slight increase in extensional viscosity at longer times at lower extension rates, instead approaching a constant. More advanced constitutive equations with more parameters could be used in the future to better model the data to try to account for this behavior.

4.2.3 Comparing Transient Extensional to Transient Shear Viscosity

To define the accuracy of the transient extensional data, it was compared to the transient shear data at the same rate, compound, and temperature. Figure 19 below shows the two data sets plotted on the same graph at a constant strain rate of 10s-1.

Because the early time data for the extensional testing was unattainable, it is difficult to determine whether the low strain data shows the appropriate linear viscoelastic response.

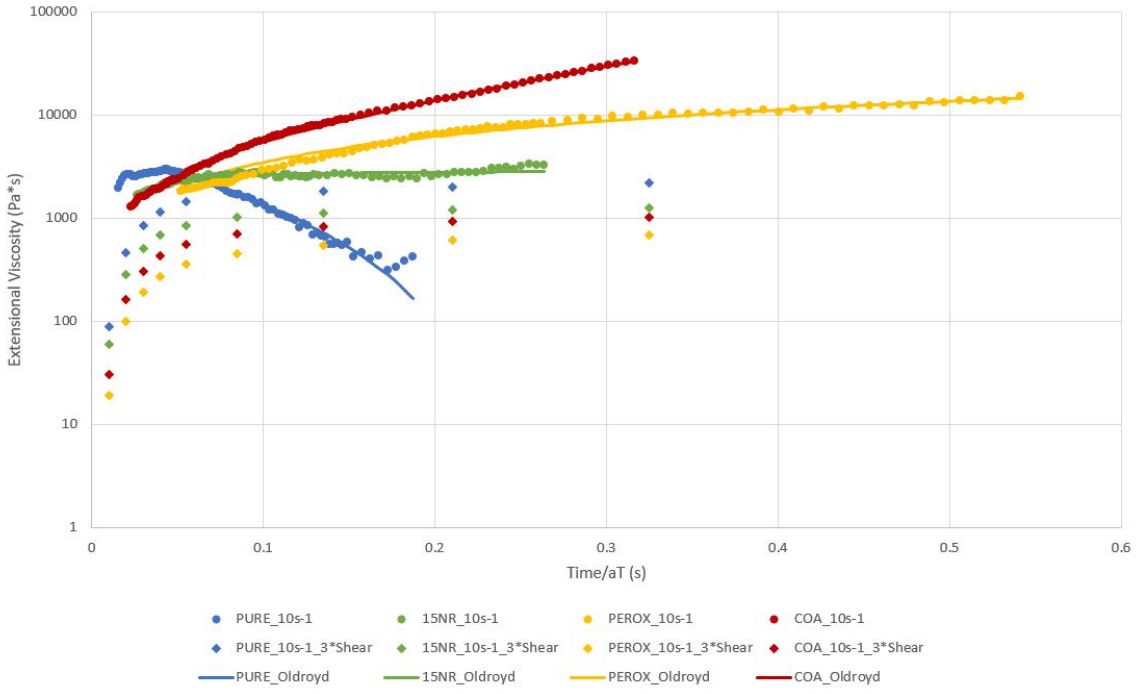

Figure 19: Comparing Transient Extensional to Transient Shear Viscosity: 10s-1, 180°C

The graph is set up so that at low strains, according to the Trouton ratio (Equation 2), the transient extensional viscosity should be the same as three times the transient shear viscosity, which is what is graphed. Ideally, a different rheometer should be used in the future to gather the extensional data to avoid this ambiguity in data accuracy. Regardless, at higher strains (longer times), the extensional viscosity increases for the blends that are designed to exhibit this behavior. To understand the effect of the extension rate on the extent of strain hardening (Equation 3), the extent of strain hardening was calculated using the peak extensional viscosity and the steady shear viscosity for each compound. The results are shown in Figures 20, 21, and 22 below.

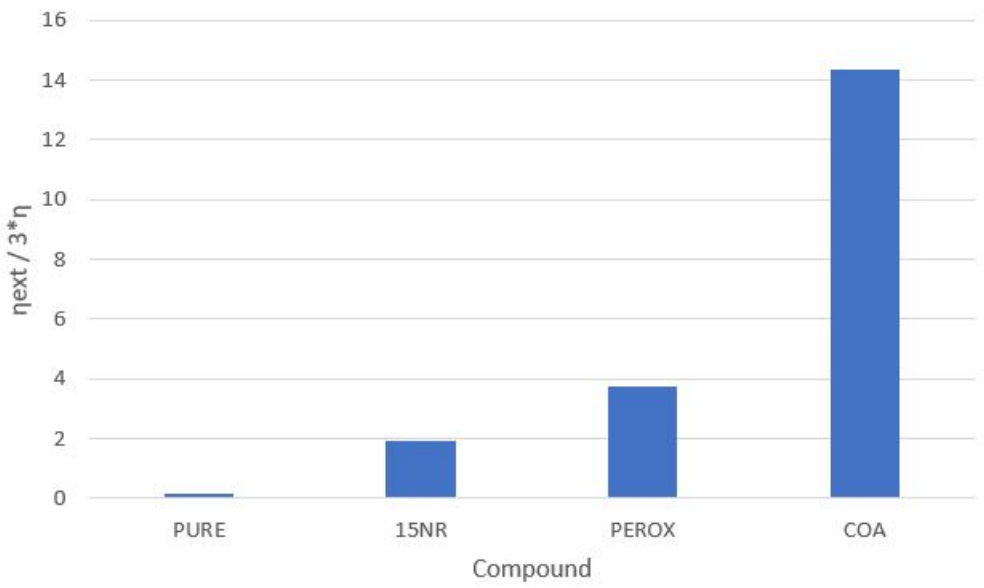

Figure 20: Extent of Strain Hardening for each Compound: 10s-1, 180°C

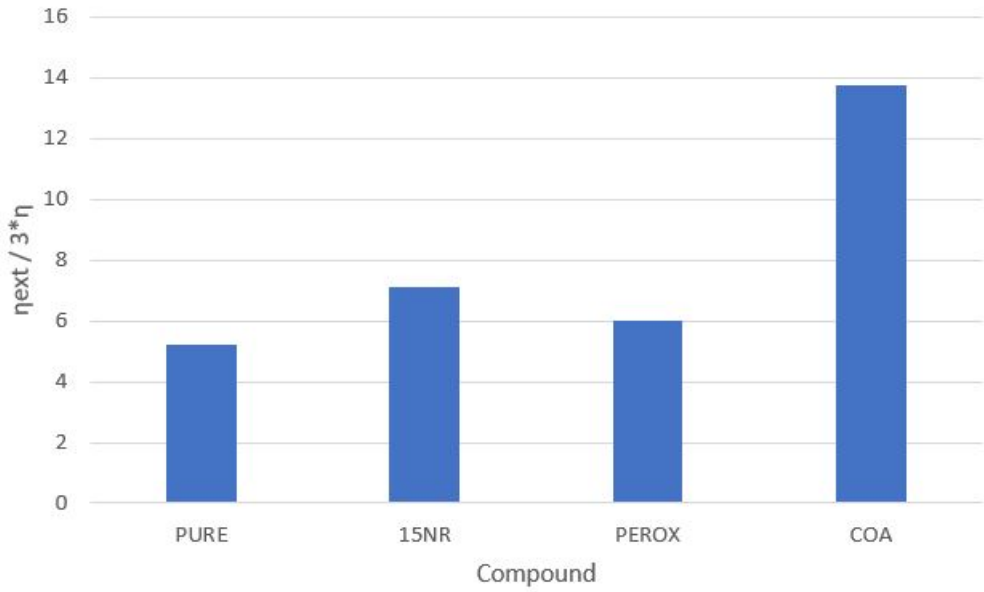

Figure 21: Extent of Strain Hardening for each Compound: 5s-1, 180°C

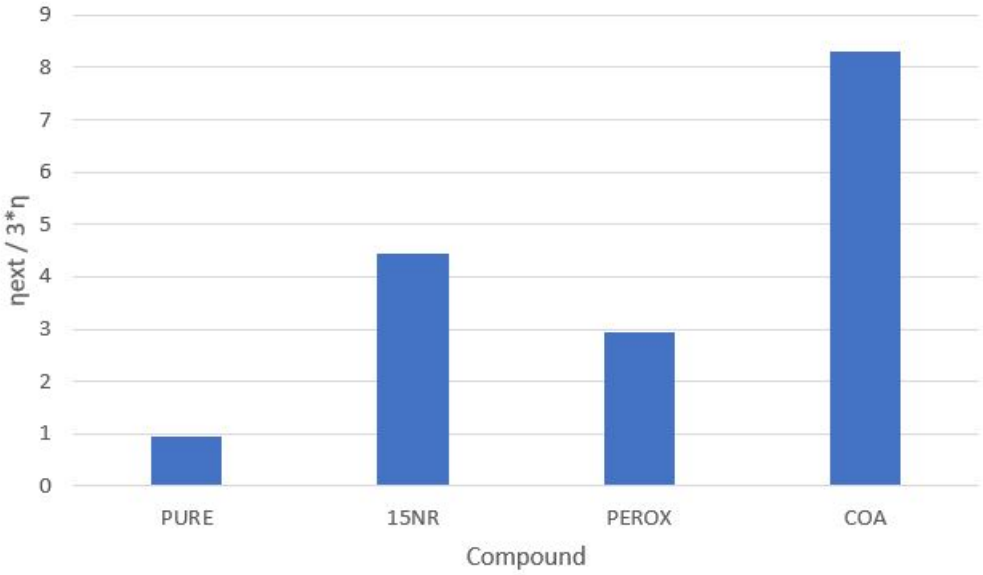

Figure 22: Extent of Strain Hardening for each Compound: 3s-1, 180°C

At each strain rate, it is clear that the COA compound exhibits the highest degree of strain hardening behavior, but its dominance diminishes at lower stretching rates. At 10s-1, the trend is exactly as hypothesized, where the amount of high structure introduced into the polymer in the form of long chain branching or crosslinking determines the extent of strain hardening, with more structure leading to more strain hardening. However, at 5 and 3s-1, there is no trend in these three compounds. This suggests that the combination of the final strain of 3.4 and the stretching rate of 10s-1 takes each of the compounds well outside the linear viscoelastic regime, while below 5s-1 the compounds might be closer to the edge so their non-linear behavior is not as prevalent.

5 Conclusions and Future Work

5.1 Summary

The extensional rheology of Pure PHBV and 3 PHBV compounds previously synthesized by Zhao was characterized using a unique methodology approach to overcome the challenges associated with measuring extensional flow using a lower molecular weight, and consequently lower viscosity material like PHBV. To overcome temperature control ambiguity, a lumped system analysis was conducted to approximate the sample's temperature based on the oven temperature reading and thermal properties of PHBV retrieved from the literature. To validate the assumptions associated with using a lumped system analysis, the sample's Biot number was calculated and found to be less than 0.1 for all sample thicknesses, satisfying the requirement of having a uniform sample temperature. To present these calculated sample temperatures at the same temperature to allow for meaningful viscosity comparisons, dynamic shear data was conducted on the same compounds to obtain shift factors using the WLF equation and the principle of time-temperature superposition. Because only one of the compounds successfully fit the WLF equation to its shifted data, the WLF constants $C1$ and $C2$ calculated for that compound were used for all the others as an approximation. The transient extensional viscosity data was shifted vertically and horizontally based on these shift factors and compared to transient shear viscosity data to quantify the degree of strain hardening in each compound for each extension rate. At the high stretching rate of 10s-1, the compounds exhibited the expected pattern based on the amount of long chain branching/crosslinks in their structure, with PHBV showing the least followed by 15NR, PEROX and finally COA showing the most strain hardening. At lower stretching rates of 5 and 3s-1, while the COA still shows the most strain hardening, the differences between the other three compounds are no longer noticeable. This suggests that future extensional viscosity characterization used to predict strain hardening behavior should be conducted at high stretching rates to allow the compounds to distin-

guish themselves well outside of the linear viscoelastic regime. This extensional rheology characterization can be applied to any new compounds of interest in food science and biodegradability to evaluate their potential in applications that would require film blowing or blow molding, such as food packaging.

5.2 Future Work

While the data presented in this thesis was repeatable, it has not been replicated by more than one operator. An essential next step if the method is to be validated is to ensure that the results are not exclusive to one operator, specifically with regards to the extensional viscosity testing. Additionally, more direct characterization of the compounds that were studied should be conducted in-house to attain a better understanding of what exactly the material is. Tabulated information online is only an approximation because of the company to company and lot to lot variation associated with polymer synthesis. Specifically, the heat capacity and thermal conductivity should be measured, along with the molecular weight and molecular weight distribution using gel permeation chromatography (GPC). Next, a more advanced non-linear constitutive model should be applied to the extensional viscosity data in an attempt to account for the extensional thinning behavior in the PURE PHBV at higher extension rates, as well as the non-constant extensional viscosity in all of the compounds at lower extension rates. Lastly, further modifications should be made to the PHBV to see if the extensional rheological characterization continues to accurately predict the strain hardening behavior outside of the design space explored in this thesis.

5.3 Additional Applications

Ideally, the methodology described in this thesis for characterizing the extensional viscosity of lower viscosity compounds could be applied to any new polymer to be used for an extensional processing regime, such as other biodegradable polymers for food packaging.

Work in the literature has demonstrated the ability of extensional viscosity testing to predict melt flow stability when subjected to extensional flow regimes, an essential behavior to help with process speed and product uniformity. When using some of the analysis models and equations applied in this thesis, it is important to consider whether the research scenario and compound of interest warrant/justify such an analysis, notably using a lumped system analysis and the WLF equation.

5.4 Contributions

The majority of the testing conducted for this thesis was performed by Peter Dent and Dr. Xiaoying Zhao. Dr. Kurt Koelling and Dr. Osvaldo Campanella provided guidance on the rheological analysis and operation of the Discovery HR-3 and ARES-LS2 rheometers. Dr. Yael Vodovotz worked with Dr. Xiaoying Zhao to establish the collaborations for this project. The thesis was written and defended by Peter Dent, in front of his advisor, Dr. Kurt Koelling, and Dr. Osvaldo Campanella.

6 Notation

6.1 Acronyms

PHBV - Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

PHA - Poly(hydroxyalkane)

PHB - Polyhydroxybutyrate

HV - Poly-3-hydroyxyvalerate

PLA - Poly-lactic acid

HMW - High Molecular Weight

NR - Natural Rubber

SEM - Scanning Electron Microscopy

TMPTA - Trimethylol propane triacrylate

PURE - Pure PHBV compound, see Table 2.

15NR - Blend of PHBV w/15 weight percent natural rubber, see Table 2.

PEROX - Blend of PHBV w/15 weight percent natural rubber and a peroxide curing system, see Table 2.

COA - Blend of PHBV w/15 weight percent natural rubber, a peroxide curing system, and a coagent to promote crosslinking between the natural rubber and PHBV, see Table 2.

Tg - Polymer Glass Transition Temperature

Tm - Melting Point Temperature

WLF - Williams-Landel-Ferry, usually referring to the time-temperature superposition relation, see Equation 5.

LDPE - Low Density Polyethylene

TRIOS - Test creation software used by TA Instruments

PRT - Platinum Resistance Thermometer

DE - Deleware

USA - United States of America

HR-3 - Hybrid Rheometer 3

SER3 - Sentmanat Extension Rheometer

GPC - Gel Permeation Chromatography

DSC - Differential Scanning Calorimetry

6.2 Units

cm - Centimeters

mm - Millimeters

m - Meters

s - Seconds

min - Minutes

K - Kelvin

C - Celsius

kg - Kilogram

g - Grams

J - Joule

W - Watt

Pa - Pascal

$wt\%$ - weight percent

PHR - Parts per 100 Rubber

Hz - Hertz

μ - micro

N - Newton

6.3 Variables

C_1 - WLF Parameter

C_2 - WLF Parameter

aT - WLF shift factor

G' - Storage Modulus

G'' - Loss Modulus

τ - Shear Stress

η - Shear Viscosity

η_E - Extensional Viscosity

$\eta_{E,max}$ - Maximum/steady state extensional viscosity

η_0 - Zero-shear viscosity

η_∞ - Steady-shear viscosity

$\dot{\gamma}$ - Shear rate

C_p - Constant Pressure Heat Capacity

k - Thermal Conductivity

h - Convective Heat Transfer Coefficient

E_η - Activation Energy

R - Gas Constant

T - Absolute Temperature

T_r - Reference Absolute Temperature

η_r - Reference Viscosity

ρ - Density

ρ_r - Reference Density

L - Characteristic Length

Bi - Biot Number

$T(t)$ - Sample Temperature as a Function of Time

T_∞ - Oven Temperature

T_i - Initial Sample Temperature for each Iteration

b - Lumped Exponential Decay Constant

A - Sample Surface Area

V - Sample Volume

$\lambda 1$ - Relaxation Time

$\lambda 2$ - Retardation Time

$3\eta_0$ - Value of extensional viscosity predicted by Oldroyd-B at steady state and low extension rate $\dot{\epsilon}$ - Extension Rate D - Rate of Deformation Tensor

$\overset{\triangledown}{D}$ - Upper Convected Time Derivative of D

$\overset{\triangledown}{\tau}$ - Upper Convected Time Derivative of τ

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8 Appendix: Supplementary Figures

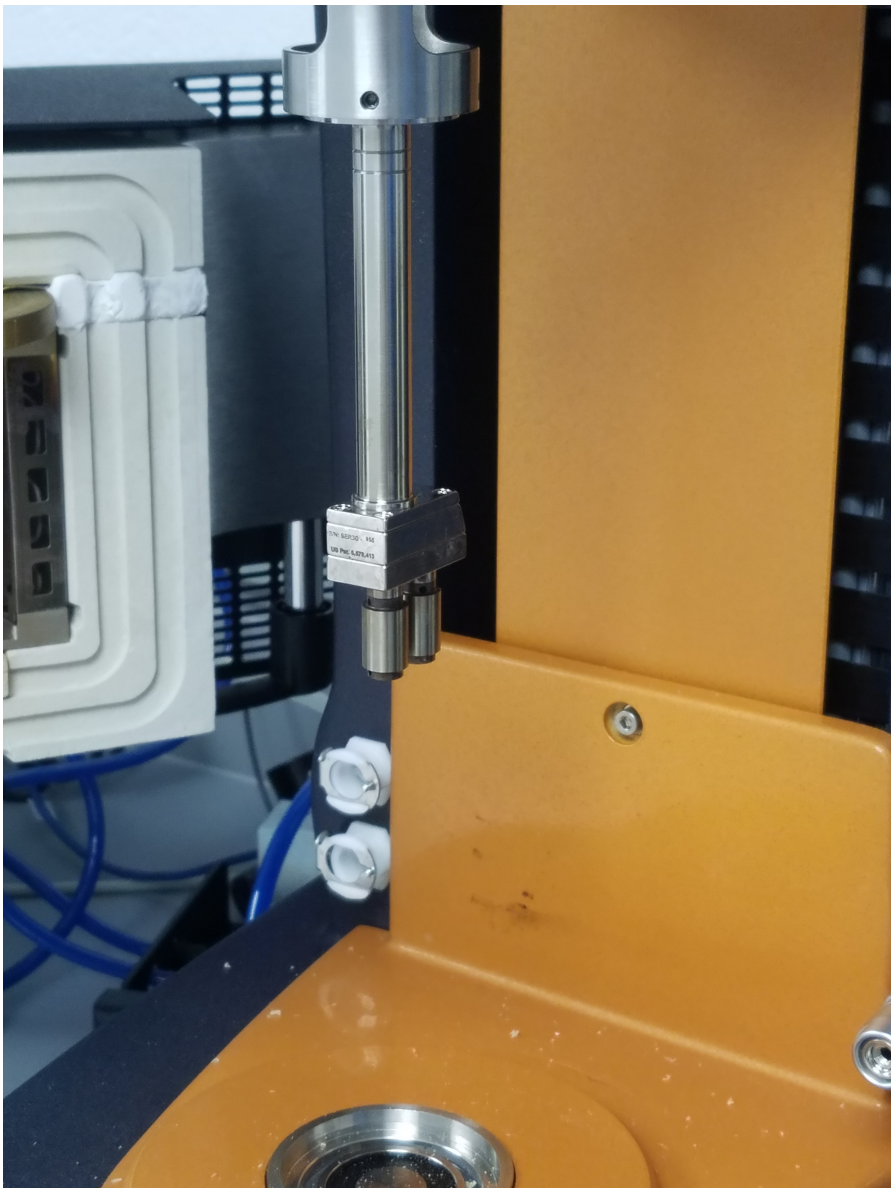

Figure 23: Discovery HR-3 Rheometer with SER Attachment

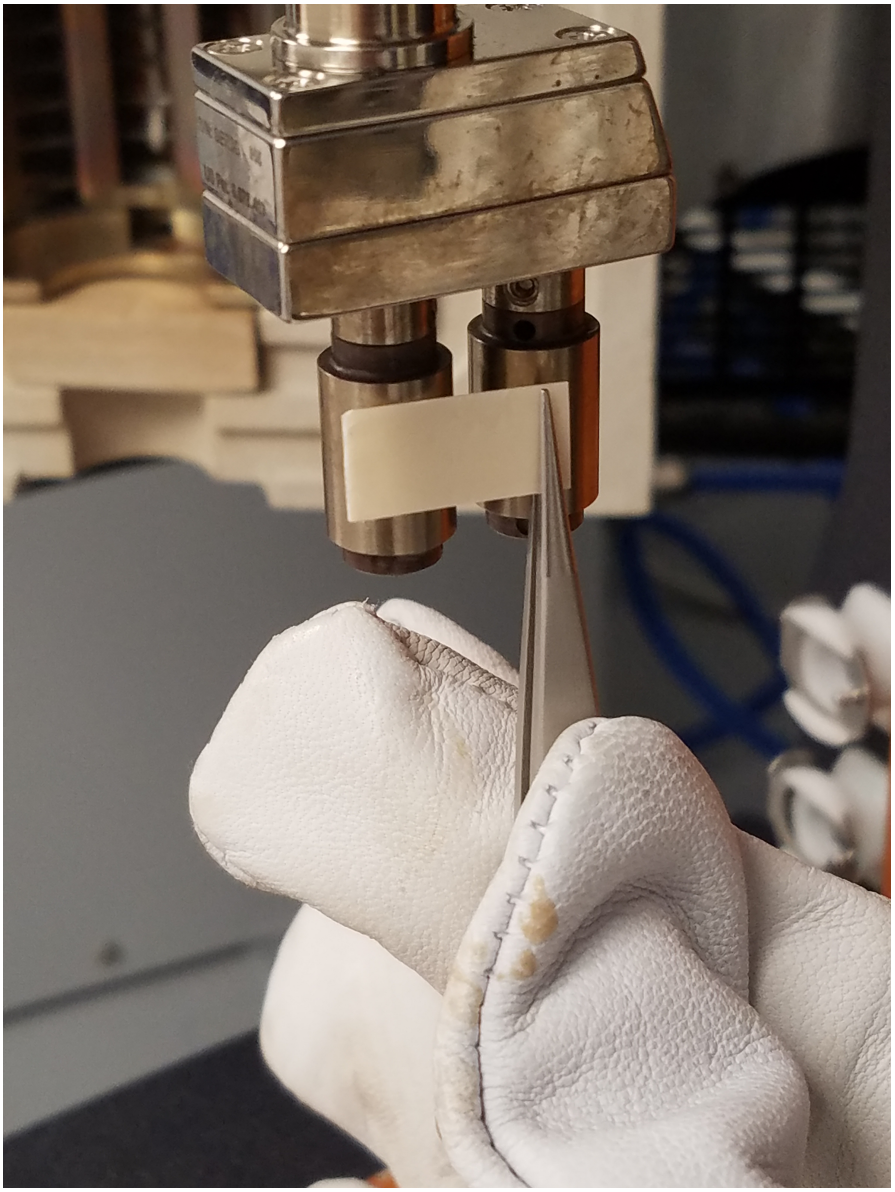

Figure 24: Mounting a Sample onto the Pre-Heated Drums

Figure 25: Successful Extension: Width Reduction is Uniform Throughout